Enantioselective Nucleophile-Catalyzed Synthesis of Tertiary Alkyl Fluorides via the α-Fluorination of Ketenes: Synthetic and Mechanistic Studies

Sarah Yunmi Lee, Stefan Neufeind, and Gregory C. Fu*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information

Table of Contents

I. General Information

Unless otherwise noted, all materials were purchased from commercial suppliers. *N*-fluorobenzenesulfonimide (NFSI) was purchased from either Alfa Aesar or Oakwood Chemicals and purified by recrystallization from dichloromethane/hexanes prior to use. Both enantiomers of **PPY*** are commercially available from Strem Chemicals (catalog numbers 26-3700 and 26-3701).

Aryl alkyl ketenes were synthesized by the dehydrohalogenation of the corresponding acid chlorides.[1] Isopropyl methyl ketene was prepared from the corresponding α-bromo acid bromide.[2] THF was purified prior to use by passage through a column of neutral alumina under argon.

HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALCEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μ). Chiral GC data

(1) (a) Zuhl, A. M.; Mohr, J. T.; Bachovchin, D. A.; Niessen, S.; Hsu, K.-L.; Berlin, J. M.; Dochnahl, M.; López-Alberca, M. P.; Fu, G. C.; Cravatt, B. F. *J. Am. Chem. Soc.* **2012**, *134*, 5068–5071. (b) Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 10006–10007. (c) Allen, A. D.; Baigrie, L. M.; Gong, L.; Tidwell, T. T. *Can. J. Chem.* **1991**, *69*, 138–145.

(2) Wilson, J. E.; Fu, G. C. *Angew. Chem. Int. Ed.* **2004**, *43*, 6358–6360.

were obtained on an Agilent 6850 series system equipped with a Varian CP-Chirasil-DEX CB column.

II. Preparation of C_6F_5ONa

Sodium pentafluorophenoxide. In a nitrogen-filled glovebox, a solution of pentafluorophenol (4.60 g, 25.0 mmol) in THF (7.50 mL) was added dropwise over 60 seconds to a round-bottom flask that contained NaH (0.60 g, 25.0 mmol) in THF (7.5 mL). The reaction mixture was stirred at r.t. for 30 min, and then it was concentrated under reduced pressure, furnishing the desired product as a white powder. The powder was dried under high vacuum (250 mtorr) overnight and used without further purification.

^{19}F NMR (282 MHz, acetone-d_6) δ –173.2 (m), –173.6 (m), –192.3 (m).

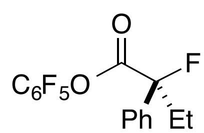
FT-IR (neat) 3659, 3233, 2360, 1616, 1502, 1460, 1377, 1274, 1247, 1164, 994, 727 cm^{-1}.

III. Catalytic Asymmetric Synthesis of Tertiary Alkyl Fluorides

General Procedure 1 (glovebox-free). NFSI (126 mg, 0.400 mmol; note: NFSI should be recrystallized from dichloromethane/*n*-hexanes before use) was added to an oven-dried 100-mL round-bottom flask equipped with a stir bar. The flask was capped with a rubber septum, and then it was evacuated and backfilled with nitrogen (three cycles); next, THF (32 mL) was added via syringe. (–)-**PPY*** (4.5 mg, 0.012 mmol) was added to an oven-dried 4-mL vial, and this vial was capped, and then it was evacuated and backfilled with nitrogen (three cycles); next, THF (0.40 mL) was added via syringe. C_6F_5ONa (82.4 mg, 0.400 mmol) was added to an oven-dried 20-mL vial, and this vial was capped, and then it was evacuated and backfilled with nitrogen (three cycles); next, THF (8.0 mL) was added via syringe. Another 20-mL vial was evacuated and backfilled with nitrogen (three cycles); next, ketene (0.400 mmol) and THF (8.0 mL) were added in turn via syringe. A nitrogen-filled balloon was attached to the flask that contained the NFSI solution, which was then cooled to –78 °C, and the solution of (–)-**PPY*** was added to the flask via syringe. Then, the ketene (8.0 mL of a 0.050 M solution in THF; 0.40 mmol) and C_6F_5ONa (8.0 mL of a 0.050 M solution in THF; 0.40 mmol) were added to the 100-mL round-bottom flask dropwise simultaneously via syringe pump over 2 h (Note: the needles should be aligned such that the C_6F_5ONa and ketene solutions do not mix prior to reaching the reaction mixture). The reaction mixture was stirred at –78 °C for an additional 2 h, and then it was concentrated under reduced pressure. To remove the (–)-**PPY*** and $NaN(SO_2Ph)_2$, the residue was dissolved in CH_2Cl_2 (5.0 mL) and filtered through a pad of silica (eluted with CH_2Cl_2 (20 mL)). The solution was concentrated, and the product was purified by column chromatography (hexanes → 10% Et_2O in hexanes; $KMnO_4$ stain).

Notes: (a) The ee of the product was determined after transesterification to the corresponding phenyl ester (conditions: 1.5 equiv PhOH, 2.0 equiv Et_3N; THF (0.1 M in ester); 12 h at r.t.). (b) For the ketene illustrated in Entry 1 of Table 2, the fluorination proceeded in 86% ee and 98% yield when the ketene and C_6F_5ONa solutions were added dropwise over 1 min, rather than by syringe pump over 2 h. (c) The amount of hydrodefluorination product was determined by GC analysis.

General Procedure 2 (with a glovebox; the yields and ee's are essentially identical to General Procedure 1 (vide infra). In a nitrogen-filled glovebox, NFSI (126 mg, 0.400 mmol; NFSI should be recrystallized from dichloromethane/*n*-hexanes before use) and THF (32 mL) were combined in an oven-dried 100-mL round-bottom flask equipped with a stir bar. The flask was fitted with a rubber septum and then removed from the glovebox. A nitrogen-filled balloon was attached to the flask, which was then cooled to –78 °C, and then a solution of (–)-**PPY*** (4.5 mg in THF (0.40 mL); 0.012 mmol) was added to the flask via syringe. Then, the ketene (8.0 mL of a 0.050 M solution in THF; 0.40 mmol) and C_6F_5ONa (8.0 mL of a 0.050 M solution in THF; 0.40 mmol) were added dropwise to the flask simultaneously via syringe pump over 2 h (Note: the needles should be aligned such that the C_6F_5ONa and ketene solutions do not mix prior to reaching the reaction mixture). The reaction mixture was stirred at –78 °C for an additional 2 h, and then it was concentrated under reduced pressure. To remove the (–)-**PPY*** and $NaN(SO_2Ph)_2$, the residue was dissolved in CH_2Cl_2 (5.0 mL) and filtered through a pad of silica (eluted with CH_2Cl_2 (10 mL)). The solution was concentrated, and the product was purified by column chromatography (hexanes → 10% Et_2O in hexanes; $KMnO_4$ stain).



(*S*)-Perfluorophenyl 2-fluoro-2-phenylbutanoate (Table 2, entry 1). The title compound was prepared according to General Procedure 2, using phenyl ethyl ketene (58.5 mg, 0.400 mmol). After purification by flash chromatography (eluted with hexanes → 10% Et_2O in hexanes), the title compound was isolated as a colorless oil (135 mg, 97% yield; contained 1% perfluorophenyl 2-phenylbutanoate) with 99% ee.

The ee of the product was determined after transesterification to phenyl 2-fluoro-2-phenylbutanoate (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: hexanes; 1.0 mL/min; retention times: 34.5 min (major), 51.2 min (minor)).

The second run was performed with (+)-**PPY*** according to General Procedure 1. The product was isolated as a colorless oil (137 mg, 99% yield; contained 1% perfluorophenyl 2-phenylbutanoate) with 98% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59–7.56 (m, 2H), 7.47–7.40 (m, 3H), 2.63–2.53 (m, 1H), 2.37–2.29 (m, 1H), 1.12 (t, 3H, J = 7.5 Hz).

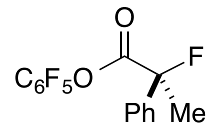
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 141.1 (dm, J_{CF} = 253 Hz), 139.8 (dm, J_{CF} = 250 Hz), 137.9 (dm, J_{CF} = 246 Hz), 136.6, 129.2, 128.7, 124.8, 124.5, 97.5 (d, J_{CF} = 193 Hz), 31.2, 7.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ –152.3 (m), –157.0 (t, J = 22 Hz), –161.8 (m), –164.7 (dd, J = 19 Hz, J = 28 Hz).

FT-IR (neat) 2929, 2855, 1801, 1783, 1653, 1521, 1496, 1464, 1451, 1387, 1344, 1299, 1208, 1149, 1110, 1087, 998, 911, 843, 765, 722, 714 cm^{-1}.

MS (FAB) *m/z* (M+Na$^+$) calcd for $C_{16}H_{10}F_6NaO_2$: 371, found: 371.

$[\alpha]^{25}_D$ = +11 (c = 1.0, $CHCl_3$; obtained with (+)-**PPY***).



(*S*)-Perfluorophenyl 2-fluoro-2-phenylpropanoate (Table 2, entry 2). The title compound was prepared according to General Procedure 1, using phenyl methyl ketene (52.9 mg, 0.400 mmol). After purification by flash chromatography (eluted with hexanes → 10% Et_2O in hexanes), the title compound was isolated as a light-yellow oil (124 mg, 93% yield; contained 2% perfluorophenyl 2-phenylpropanoate) with 98% ee.

The ee of the product was determined after transesterification to phenyl 2-fluoro-2-phenylpropanoate (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: hexanes; 1.0 mL/min; retention times: 57.0 min (major), 70.1 min (minor)).

The second run was performed with (+)-**PPY*** according to General Procedure 1. The product was isolated as a light-yellow oil (122 mg, 91% yield; contained 2% perfluorophenyl 2-phenylpropanoate) with 97% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.58 (m, 2H), 7.48–7.43 (m, 3H), 2.13 (d, 3H, J = 22.0 Hz).

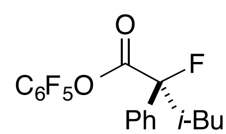
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 140.9 (dm, J_{CF} = 251 Hz), 139.8 (dm, J_{CF} = 250 Hz), 137.8 (dm, J_{CF} = 247 Hz), 137.4, 129.4, 128.8, 124.7, 124.6, 94.6 (d, J_{CF} = 188 Hz), 24.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ –149.5 (q, J = 23 Hz), –152.6 (m), –157.0 (t, J = 22 Hz), –161.9 (m).

FT-IR (neat) 2995, 1787, 1724, 1521, 1497, 1472, 1449, 1378, 1228, 1148, 1090, 1068, 1029, 994, 914, 773, 726 cm^{-1}.

MS (EI) *m/z* (M–F$^+$) calcd for $C_{15}H_8F_5O_2$: 315, found: 315.

$[\alpha]^{25}_D$ = +74 (c = 1.0, $CHCl_3$; obtained with (+)-**PPY***).



(*S*)-Perfluorophenyl 2-fluoro-4-methyl-2-phenylpentanoate (Table 2, entry 3). The title compound was prepared according to General Procedure 1, using phenyl isobutyl ketene (69.7 mg, 0.400 mmol). After purification by flash chromatography (eluted with hexanes → 10% Et_2O in hexanes), the title compound was isolated as a colorless oil (143 mg, 95% yield; contained 1% perfluorophenyl 4-methyl-2-phenylpentanoate) with 94% ee.

The ee of the product was determined after transesterification to phenyl 2-fluoro-4-methyl-2-phenylpentanoate (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: hexanes; 1.0 mL/min; retention times: 15.2 min (minor), 28.7 min (major)).

The second run was performed with (+)-**PPY*** according to General Procedure 2. The product was isolated as a colorless oil (143 mg, 95% yield; contained 1% perfluorophenyl 4-methyl-2-phenylpentanoate) with 96% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.58 (m, 2H), 7.45–7.42 (m, 3H), 2.53–2.43 (m, 1H), 2.29–2.21 (m, 1H), 1.97 (septet, 1H, J = 5.0 Hz), 1.06–1.02 (m, 6H).

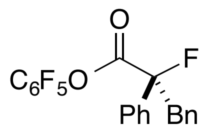
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 141.0 (dm, J_{CF} = 254 Hz), 139.8 (dm, J_{CF} = 248 Hz), 137.8 (dm, J_{CF} = 243 Hz), 137.3, 129.1, 128.7, 124.6, 124.5, 97.4 (d, J_{CF} = 193 Hz), 46.1, 24.7, 23.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ –152.3 (m), –157.1 (t, J = 22 Hz), –161.9 (m), –162.9 (dd, J = 20 Hz, J = 31 Hz).

FT-IR (neat) 2961, 1785, 1718, 1653, 1559, 1520, 1472, 1450, 1199, 1100, 1073, 1010, 997, 725 cm^{-1}.

MS (EI) *m/z* (M–F^+) calcd for $C_{18}H_{14}F_5O_2$: 357, found: 357.

$[\alpha]^{25}_D$ = +14 (c = 1.0, $CHCl_3$; obtained with (+)-**PPY***).



(*S*)-Perfluorophenyl 2-fluoro-2,3-diphenylpropanoate (Table 2, entry 4). The title compound was prepared according to General Procedure 1, using phenyl benzyl ketene (83.3 mg, 0.400 mmol). After purification by flash chromatography (eluted with hexanes → 10% Et_2O in hexanes), the title compound was isolated as a white solid (159 mg, 97% yield; contained 3% perfluorophenyl 2,3-diphenylpropanoate) with 78% ee.

The ee of the product was determined after transesterification to phenyl 2-fluoro-2,3-diphenylpropanoate (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: hexanes; 1.0 mL/min; retention times: 53.6 min (major), 70.6 min (minor)).

The second run was performed with (+)-**PPY*** according to General Procedure 1. The product was isolated as a white solid (156 mg, 95% yield; contained 2% perfluorophenyl 2,3-diphenylpropanoate) with 77% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.47–7.42 (m, 3H), 7.31–7.26 (m, 5H), 3.82 (dd, 1H, J = 14.8 Hz, J = 30 Hz), 3.57 (dd, 1H, J = 14.8 Hz, J = 19.6 Hz).

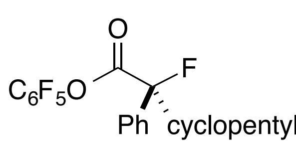
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 140.9 (dm, J_{CF} = 251 Hz), 139.8 (dm, J_{CF} = 250 Hz), 137.8 (dm, J_{CF} = 247 Hz), 136.5, 133.1, 130.5, 129.3, 128.8, 128.4, 127.5, 124.7, 124.4, 97.0 (d, J_{CF} = 195 Hz), 44.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ –151.8 (m), –157.0 (t, J = 21 Hz), –161.3 (dd, J = 20 Hz, J = 31 Hz), –161.9 (m).

FT-IR (neat) 2360, 1782, 1653, 1521, 1496, 1469, 1456, 1449, 1427, 1257, 1174, 1142, 1118, 1101, 1080, 1029, 995, 985, 916, 849, 769, 726 cm^{-1}.

MS (EI) *m/z* (M–F^+) calcd for $C_{21}H_{12}F_6O_2$: 391, found: 391.

$[\alpha]^{25}_D$ = +17 (c = 1.0, $CHCl_3$; obtained with (+)-**PPY***).



(*S*)-Perfluorophenyl 2-cyclopentyl-2-fluoro-2-phenylacetate (Table 2, entry 5). The title compound was prepared according to General Procedure 1, using phenyl cyclopentyl ketene (74.5 mg, 0.400 mmol) and 10% (–)-**PPY*** (15.1 mg, 0.0400 mmol). Reaction time: 12 h. After purification by flash chromatography (eluted with hexanes → 10% Et_2O in hexanes), the title compound was isolated as a colorless oil (130 mg, 84% yield; contained 1% perfluorophenyl 2-cyclopentyl-2-phenylacetate) with 79% ee.

The ee of the product was determined after transesterification to phenyl 2-cyclopentyl-2-fluoro-2-phenylacetate (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: hexanes; 1.0 mL/min; retention times: 23.4 min (major), 36.1 min (minor)).

The second run was performed with (+)-**PPY*** according to General Procedure 1. The product was isolated as a colorless oil (130 mg, 84% yield; contained 1% perfluorophenyl 2-cyclopentyl-2-phenylacetate) with 80% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.45–7.38 (m, 3H), 3.15 (doublet of quintets, 1H, J = 34.0 Hz, J = 8.5 Hz), 1.99–1.92 (m, 1H), 1.86–1.74 (m, 2H), 1.71–1.63 (m, 2H), 1.60–1.51 (m, 2H), 1.50–1.41 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 141.0 (dm, J_{CF} = 254 Hz), 139.8 (dm, J_{CF} = 247 Hz), 137.8 (dm, J_{CF} = 245 Hz), 136.7, 128.9, 128.6, 124.9, 124.4, 98.3 (d, J_{CF} = 195 Hz), 46.0, 26.7, 26.2.

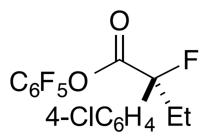
^{19}F NMR (282 MHz, $CDCl_3$) δ –152.3 (m), –157.2 (t, J = 22 Hz), –162.0 (m), –177.9 (d, J = 34 Hz).

FT-IR (neat) 2962, 2874, 2670, 2463, 1799, 1784, 1654, 1520, 1472, 1450, 1359, 1318, 1207, 1159, 1075, 1011, 998, 957, 910, 879, 840, 754, 715 cm^{-1}.

MS (EI) m/z (M–F^+) calcd for $C_{19}H_{14}F_5O_2$: 369, found: 369.

$[\alpha]^{25}_{D}$ = –46 (c = 1.0, $CHCl_3$; obtained with (+)-**PPY***).

$[\alpha]^{25}_{D}$ = +41 (c = 1.0, $CHCl_3$; obtained with (–)-**PPY***).



(*S*)-Perfluorophenyl 2-(4-chlorophenyl)-2-fluorobutanoate (Table 2, entry 6). The title compound was prepared according to General Procedure 1, using 4-chlorophenyl ethyl ketene (72.2 mg, 0.400 mmol). After purification by flash chromatography (eluted with hexanes → 10% Et_2O in hexanes), the title compound was isolated as a colorless oil (134 mg, 88% yield; contained 3% perfluorophenyl 2-(4-chlorophenyl)butanoate) with 96% ee.

The ee of the product was determined after transesterification to phenyl 2-(4-chlorophenyl)-2-fluorobutanoate (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: hexanes; 1.0 mL/min; retention times: 44.5 min (minor), 63.1 min (major)).

The second run was performed with (+)-**PPY*** according to General Procedure 1. The product was isolated as a colorless oil (129 mg, 84% yield; contained 3% perfluorophenyl 2-(4-chlorophenyl)butanoate) with 98% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.50 (m, 2H), 7.45–7.40 (m, 2H), 2.66–2.45 (m, 1H), 2.39–2.20 (m, 1H), 1.11 (t, 3H, J = 7.5 Hz).

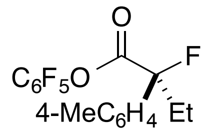
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 140.9 (dm, J_{CF} = 250 Hz), 139.9 (dm, J_{CF} = 252 Hz), 137.9 (dm, J_{CF} = 252 Hz), 135.4, 135.1, 129.0, 126.3, 124.4, 97.1 (d, J_{CF} = 193 Hz), 31.3, 7.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ –152.4 (m), –156.8 (t, J = 20 Hz), –161.7 (m), –165.0 (dd, J = 20 Hz, J = 28 Hz).

FT-IR (neat) 2983, 2944, 2360, 1802, 1785, 1653, 1598, 1521, 1493, 1462, 1403, 1360, 1299, 1207, 1150, 1095, 998, 909, 825, 747, 714 cm^{-1}.

MS (EI) m/z (M–F^+) calcd for $C_{16}H_9ClF_5O_2$: 363, found: 363.

$[\alpha]^{25}{}_D$ = –5.3 (c = 2.0, $CHCl_3$; obtained with (–)-**PPY***).



(*S*)-Perfluorophenyl 2-fluoro-2-(*p*-tolyl)butanoate (Table 2, entry 7). The title compound was prepared according to General Procedure 1, using *p*-tolyl ethyl ketene (64.1 mg, 0.400 mmol). After purification by flash chromatography (eluted with hexanes → 10% Et_2O in hexanes), the title compound was isolated as a colorless oil (135 mg, 93% yield; contained 5% perfluorophenyl 2-(*p*-tolyl)butanoate) with 97% ee.

The ee of the product was determined after transesterification to phenyl 2-fluoro-2-(*p*-tolyl)butanoate (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: hexanes; 1.0 mL/min; retention times: 39.7 min (minor), 48.7 min (major)).

The second run was performed with (+)-**PPY*** according to General Procedure 2. The product was isolated as a colorless oil (132 mg, 91% yield; contained 5% perfluorophenyl 2-(p-tolyl)butanoate) with 97% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2H), 7.17–7.15 (m, 2H), 2.54–2.41 (m, 1H), 2.29 (s, 3H), 2.27–2.17 (m, 1H), 1.03 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 141.0 (dm, J_{CF} = 255 Hz), 139.7 (dm, J_{CF} = 251 Hz), 139.2, 137.8 (dm, J_{CF} = 244 Hz), 133.6, 129.4, 124.7, 124.5, 97.5 (d, J_{CF} = 192 Hz), 31.1, 21.1, 7.4.

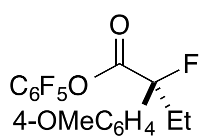
^{19}F NMR (282 MHz, $CDCl_3$) δ –152.3 (m), –157.1 (t, *J* = 22 Hz), –162.0 (m), –163.6 (dd, *J* = 19 Hz, *J* = 29 Hz).

FT-IR (neat) 2982, 2944, 2360, 1800, 1783, 1654, 1462, 1300, 1205, 1150, 1107, 1085, 1023, 998, 907, 814, 736 cm^{-1}.

MS (EI) *m/z* (M–F^+) calcd for $C_{17}H_{12}F_5O_2$: 343, found: 343.

$[\alpha]^{25}{}_D$ = –13 (c = 1.0, $CHCl_3$; obtained with (+)-**PPY***).

$[\alpha]^{25}{}_D$ = +11 (c = 1.0, $CHCl_3$; obtained with (–)-**PPY***).



(*S*)-Perfluorophenyl 2-fluoro-2-(4-methoxyphenyl)butanoate (Table 2, entry 8). The title compound was prepared according to General Procedure 1, using 4-methoxyphenyl ethyl ketene (70.5 mg, 0.400 mmol). After purification by flash chromatography (eluted with hexanes→ 10% Et_2O in hexanes), the title compound was isolated as a colorless oil (134 mg, 89% yield; contained 1% perfluorophenyl 2-(4-methoxyphenyl)butanoate) with 97% ee.

The ee of the product was determined after transesterification to phenyl 2-fluoro-2-(4-methoxyphenyl)butanoate (HPLC analysis of the product: Daicel CHIRALCEL AD-H column; solvent system: hexanes; 1.0 mL/min; retention times: 12.0 min (major), 13.6 min (minor)).

The second run was performed with (+)-**PPY*** according to General Procedure 2. The product was isolated as a colorless oil (140 mg, 93% yield; contained 1% perfluorophenyl 2-(4-methoxyphenyl)butanoate) with 97% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.49 (m, 2H), 6.98–6.94 (m, 2H), 3.84 (s, 3H), 2.62–2.52 (m, 1H), 2.37–2.29 (m, 1H), 1.13 (t, 3H, J = 7.5 Hz).

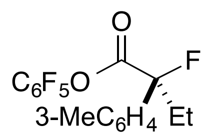
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 160.2, 141.0 (dm, J_{CF} = 253 Hz), 139.7 (dm, J_{CF} = 249 Hz), 137.8 (dm, J_{CF} = 244 Hz), 128.5, 126.3, 124.6, 114.0, 97.3 (d, J_{CF} = 192 Hz), 55.3, 30.9, 7.4.

^{19}F NMR (282 MHz, $CDCl_3$) δ –152.4 (m), –157.2 (t, J = 21 Hz), –161.8 to –162.1 (m).

FT-IR (neat) 2943, 2842, 1799, 1783, 1611, 1584, 1521, 1465, 1307, 1257, 1199, 1182, 1149, 1086, 1033, 997, 907, 829 cm^{-1}.

MS (FAB) m/z (M^+) calcd for $C_{17}H_{12}F_6O_3$: 378, found: 378.

$[\alpha]^{25}_{D}$ = +31 (c = 2.0, $CHCl_3$; obtained with (–)-**PPY***).



(*S*)-Perfluorophenyl 2-fluoro-2-(*m*-tolyl)butanoate (Table 2, entry 9). The title compound was prepared according to General Procedure 1, using *m*-tolyl ethyl ketene (64.1 mg, 0.400 mmol). After purification by flash chromatography (eluted with hexanes → 10% Et_2O in hexanes), the title compound was isolated as a colorless oil (140 mg, 97% yield; contained 2% perfluorophenyl 2-(*m*-tolyl)butanoate) with 96% ee.

The ee of the product was determined after transesterification to phenyl 2-fluoro-2-(*m*-tolyl)butanoate (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: hexanes; 1.0 mL/min; retention times: 24.0 min (minor), 43.0 min (major)).

The second run was performed with (+)-**PPY*** according to General Procedure 2. The product was isolated as a colorless oil (141 mg, 97% yield; contained 3% perfluorophenyl 2-(*m*-tolyl)butanoate) with 98% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.32 (m, 3H), 7.24–7.22 (m, 1H), 2.64–2.51 (m, 1H), 2.41 (s, 3H), 2.39–2.28 (m, 1H), 1.13 (t, 3H, J = 7.5 Hz).

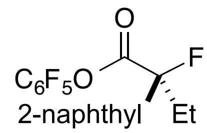
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 141.0 (dm, J_{CF} = 253 Hz), 139.8 (dm, J_{CF} = 253 Hz), 138.6, 137.9 (dm, J_{CF} = 244 Hz), 136.5, 129.9, 128.6, 125.4, 124.5, 121.8, 97.5 (d, J_{CF} = 192 Hz), 31.2, 21.5, 7.4.

^{19}F NMR (282 MHz, $CDCl_3$) δ –152.3 (m), –157.1 (t, J = 22 Hz), –161.9 (m), –164.1 (dd, J = 19 Hz, J = 28 Hz).

IR (neat) 2983, 2945, 1801, 1785, 1653, 1609, 1521, 1464, 1384, 1358, 1299, 1255, 1212, 1181, 1149, 1109, 1087, 997, 937, 906, 856, 821, 788, 729, 713 cm^{-1}.

MS (EI) m/z ($M–F^+$) calcd for $C_{17}H_{12}F_5O_2$: 343, found: 343.

$[\alpha]^{25}_{D}$ = +33 (c = 3.0, $CHCl_3$; obtained with (+)-**PPY***).



(*S*)-Perfluorophenyl 2-fluoro-2-(naphthalen-2-yl)butanoate (Table 2, entry 10). The title compound was prepared according to General Procedure 1, using 2-naphthyl ethyl ketene (78.5 mg, 0.400 mmol). After purification by flash chromatography (eluted with hexanes → 10% Et_2O in hexanes), the title compound was isolated as a colorless oil (143 mg, 90% yield; contained 2% perfluorophenyl 2-(naphthalen-2-yl)butanoate) with 94% ee.

The ee of the product was determined after transesterification to phenyl 2-fluoro-2-(naphthalen-2-yl)butanoate (HPLC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: hexanes; 1.0 mL/min; retention times: 7.44 min (major), 8.93 min (minor)).

The second run was performed with (+)-**PPY*** according to General Procedure 1. The product was isolated as a colorless oil (140 mg, 88% yield; contained 3% perfluorophenyl 2-(naphthalen-2-yl)butanoate) with 93% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.95–7.88 (m, 3H), 7.69 (m, 1H), 7.58–7.54 (m, 2H), 2.77–2.64 (m, 1H), 2.53–2.41 (m, 1H), 1.19 (t, 3H, J = 7.5 Hz).

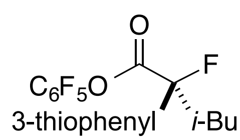
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 141.0 (dm, J_{CF} = 253 Hz), 139.8 (dm, J_{CF} = 245 Hz), 137.8 (dm, J_{CF} = 250 Hz), 133.8, 133.4, 132.9, 128.7, 128.5, 127.7, 127.0, 126.7, 124.5, 124.3, 122.1, 97.7 (d, J_{CF} = 192 Hz), 31.3, 7.4.

^{19}F NMR (282 MHz, $CDCl_3$) δ –152.2 (m), –157.0 (t, J = 22 Hz), –161.8 (m), –163.9 (dd, J = 20 Hz, J = 28 Hz).

FT-IR (neat) 3063, 2981, 2944, 1800, 1784, 1653, 1601, 1559, 1521, 1472, 1437, 1358, 1296, 1273, 1203, 1147, 1108, 1087, 997, 921, 897, 860, 817, 750, 724, 709 cm^{-1}.

MS (EI) m/z (M^+) calcd for $C_{20}H_{12}F_6O_2$: 398, found: 398.

$[\alpha]^{25}_D$ = +23 (c = 1.0, $CHCl_3$; obtained with (+)-**PPY***).



(*S*)-Perfluorophenyl 2-fluoro-4-methyl-2-(thiophen-3-yl)pentanoate (Table 2, entry 11). The title compound was prepared according to General Procedure 1, using 3-thiophenyl isobutyl ketene (72.1 mg, 0.400 mmol). After purification by flash chromatography (eluted with hexanes → 10% Et_2O in hexanes), the title compound was isolated as a light-yellow oil (143 mg, 93% yield; contained 3% perfluorophenyl 4-methyl-2-(thiophen-3-yl)pentanoate) with 96% ee.

The ee of the product was determined after transesterification to phenyl 2-fluoro-4-methyl-2-(thiophen-3-yl)pentanoate (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: hexanes; 1.0 mL/min; retention times: 21.5 min (minor), 38.0 min (major)).

The second run was performed with (+)-**PPY*** according to General Procedure 2. The product was isolated as a light-yellow oil (144 mg, 94% yield; contained 3% perfluorophenyl 4-methyl-2-(thiophen-3-yl)pentanoate) with 99% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, 1H, J = 3.3 Hz, J = 1.3 Hz), 7.40–7.38 (m, 1H), 7.21 (dd, 1H, J = 5.3 Hz, J = 1.3 Hz), 2.50–2.39 (m, 1H), 2.28–2.20 (m, 1H), 1.97 (septet, 1H, J = 6.5 Hz), 1.04 (d, 6H, J = 6.5 Hz).

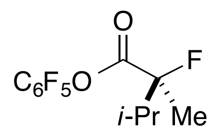
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 141.0 (dm, J_{CF} = 255 Hz), 139.8 (dm, J_{CF} = 252 Hz), 138.4, 137.8 (dm, J_{CF} = 245 Hz), 126.8, 124.8, 124.5, 122.7, 96.2 (d, J_{CF} = 192 Hz), 46.3, 24.8, 23.4.

^{19}F NMR (282 MHz, $CDCl_3$) δ –152.2 (m), –155.6 (dd, J = 18 Hz, J = 32 Hz), –156.9 (t, J = 22 Hz), –161.8 (m).

FT-IR (neat) 3118, 2962, 2875, 2671, 2464, 2360, 1800, 1785, 1653, 1520, 1370, 1276, 1203, 1181, 1146, 1117, 1099, 999, 967, 861, 840, 797, 782, 729, 708 cm^{-1}.

MS (EI) m/z ($M–F^+$) calcd for $C_{16}H_{12}F_5O_2S$: 363, found: 363.

$[\alpha]^{25}_D$ = +12 (c = 1.0, $CHCl_3$; obtained with (+)-**PPY***).



(*S*)-Perfluorophenyl 2-fluoro-2,3-dimethylbutanoate (eq 3). The title compound was prepared according to General Procedure 1, using isopropyl methyl ketene (39.3 mg, 0.400 mmol) and 10% (–)-**PPY*** (15.1 mg, 0.0400 mmol). Reaction time: 12 h. After purification by flash chromatography (eluted with hexanes → 10% Et_2O in hexanes), the title compound was isolated as a light-yellow oil (97 mg, 81% yield; contained 1% perfluorophenyl 2,3-dimethylbutanoate) with 73% ee.

The ee of the product was determined by chiral GC analysis (CP-Chirasil-DEX CB; heating program: 105 °C → 115 °C @ 1 °C/min, followed by 115 → 175 °C @ 5 °C/min; He flow rate: 1.0 mL/min; retention times: 22.4 min (minor), 23.0 min (major)).

The second run was performed with (+)-**PPY*** according to General Procedure 1. The product was isolated as a light-yellow oil (99 mg, 83% yield; contained 1% perfluorophenyl 2,3-dimethylbutanoate) with 74% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33–2.23 (m, 1H), 1.71 (d, 3H, J = 22.0 Hz), 1.10 (d, 6H, J = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 141.0 (dm, J_{CF} = 254 Hz), 139.8 (dm, J_{CF} = 246 Hz), 137.8 (dm, J_{CF} = 243 Hz), 124.5, 97.6 (d, J_{CF} = 189 Hz), 35.0, 21.3, 16.2.

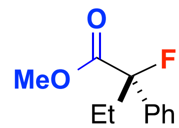
^{19}F NMR (282 MHz, $CDCl_3$) δ –152.7 (m), –157.2 (t, J = 22 Hz), –162.0 (m), –164.9 (quintet, J = 22 Hz).

IR (neat) 2980, 2887, 2671, 2463, 1804, 1787, 1655, 1524, 1471, 1394, 1379, 1360, 1247, 1211, 1169, 1148, 1110, 1064, 1008, 995, 941, 910, 868, 809, 744, 714 cm^{-1}.

MS (FAB) m/z ($M+Na^+$) calcd for $C_{12}H_{10}F_6NaO_2$: 323, found: 323.

$[\alpha]^{25}_D$ = +12 (c = 1.0, $CHCl_3$; obtained with (+)-**PPY***).

IV. Derivatizations of the Products



Transesterification: Methyl (*R*)-2-fluoro-2-phenylbutanoate. (*R*)-Perfluorophenyl 2-fluoro-2-phenylbutanoate (104 mg, 0.30 mmol; 98% ee), Et_3N (209 µL, 1.50 mmol), MeOH (1.5 mL), and THF (1.5 mL) were added to a 20-mL vial. The mixture was stirred at r.t. for 12 h, and then it was concentrated under reduced pressure. The residue was purified by column chromatography (hexanes → 10% Et_2O in hexanes), which furnished the product as a colorless oil. First run: 52 mg (88%, 98% ee). Second run: 54 mg (92%, 98% ee).

The ee of the product was determined by HPLC (Daicel CHIRALCEL AS-H column; solvent system: 1.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 6.38 min (minor), 7.77 min (major)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2H), 7.40–7.32 (m, 3H), 3.77 (s, 3H), 2.46–2.33 (m, 1H), 2.24–2.12 (m, 1H), 0.96 (t, 3H, J = 7.5 Hz).

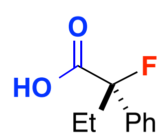
^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 138.1, 128.4, 124.7, 124.6, 97.5 (d, J_{CF} = 189 Hz), 52.8, 31.5, 7.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ –167.2 (dd, J = 21 Hz, J = 28 Hz).

FT-IR (neat) 2979, 2954, 2884, 1761, 1740, 1496, 1449, 1437, 1383, 1256, 1221, 1138, 1094, 1072, 1017, 1003, 919, 809, 770, 732 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{11}H_{13}FO_2$: 196, found: 196.

$[\alpha]^{25}_{D}$ = +17 (c = 1.0, $CHCl_3$).



Hydrolysis: (*R*)-2-Fluoro-2-phenylbutanoic acid. (*R*)-Perfluorophenyl 2-fluoro-2-phenylbutanoate (104 mg, 0.30 mmol; 98% ee), Et_3N (209 µL, 1.50 mmol), H_2O (1.5 mL), and THF (1.5 mL) were added to a 20-mL vial. The mixture was stirred at r.t. for 12 h, and then it was concentrated under reduced pressure. H_2O (5 mL) and EtOAc (5 mL) were added. The aqueous phase was brought to pH 2 by the addition of 1 N HCl. The mixture was transferred to a separatory funnel, to which EtOAc (5 mL) was added. The layers were separated, and the aqueous layer was washed with EtOAc (5 mL x2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (2.0% MeOH in CH_2Cl_2), which furnished the product as a white solid. First run: 47 mg (86%, 98% ee). Second run: 48 mg (88%, 98% ee).

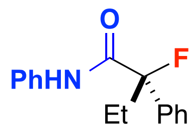
The ee of the product was determined by HPLC (Daicel CHIRALCEL OJ-H column; solvent system: 5.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 19.8 min (minor), 26.7 min (major)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.0 (br s, 1H), 7.53–7.51 (m, 2H), 7.41–7.34 (m, 3H), 2.47–2.34 (m, 1H), 2.25–2.14 (m, 1H), 0.99 (t, 3H, J = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 137.2, 128.7, 128.5, 124.8, 97.1 (d, J_{CF} = 188 Hz), 31.2, 7.4.

^{19}F NMR (282 MHz, $CDCl_3$) δ –167.2 (dd, J = 21 Hz, J = 27 Hz).

FT-IR (neat) 2925, 1728, 1497, 1450, 1220, 1142, 1071, 990, 727 cm^{-1}.
MS (EI) *m/z* (M^+) calcd for $C_{10}H_{11}FO_2$: 182, found: 182.
$[\alpha]^{25}_D = -11$ (c = 0.40, MeOH).[3]



Amidation: (*R*)-2-Fluoro-*N*,2-diphenylbutanamide. (*R*)-Perfluorophenyl 2-fluoro-2-phenylbutanoate (104 mg, 0.30 mmol; 98% ee), aniline (41.9 mg, 0.45 mmol), Et_3N (63 μL, 0.45 mmol), and THF (3.0 mL) were added to a 20-mL vial, which was then sealed with a septum cap and heated to 65 °C for 12 h. The mixture was allowed to cool to r.t., and then it was concentrated under reduced pressure. The residue was purified by column chromatography (hexanes → 10% Et_2O in hexanes), which furnished the product as a white solid. First run: 77 mg (95%, 98% ee). Second run: 75 mg (97%, 98% ee).

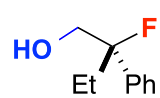
The ee of the product was determined by HPLC (Daicel CHIRALCEL OJ-H column; solvent system: 2.0% *i*-PrOH in hexanes; 1.0 mL/min; retention times: 33.3 min (minor), 35.0 min (major)).

^1H NMR (500 MHz, $CDCl_3$) δ 8.17 (br s, 1H), 7.62–7.60 (m, 2H), 7.58–7.55 (m, 2H), 7.41–7.37 (m, 2H), 7.36–7.31 (m, 3H), 7.14–7.11 (m, 1H), 2.55–2.41 (m, 1H), 2.29–2.17 (m, 1H), 1.00 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 138.4, 136.9, 129.0, 128.4, 124.8, 124.53, 124.45, 119.9, 100.4 (d, J_{CF} = 191 Hz), 31.9, 7.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ –164.9 (ddd, *J* = 20 Hz, *J* = 8.5 Hz, *J* = 30 Hz).

FT-IR (neat) 3400, 2918, 2360, 1497, 1448, 1061, 913, 878, 759 cm^{-1}.
MS (EI) *m/z* (M^+) calcd for $C_{16}H_{16}FNO$: 257, found: 257.
$[\alpha]^{25}_D = +54$ (c = 1.0, $CHCl_3$).



Reduction: (*R*)-2-Fluoro-2-phenylbutan-1-ol [188359-07-1]. $NaBH_4$ (17.0 mg, 1.45 mmol) was added to a 20-mL vial that contained (*R*)-perfluorophenyl 2-fluoro-2-phenylbutanoate (104 mg, 0.30 mmol; 98% ee) and THF (3.0 mL). The mixture was stirred at r.t. for 4 h, and then H_2O (0.2 mL) was added. The mixture was transferred to a separatory funnel, to which Et_2O (5 mL) and H_2O (1 mL) were added. The layers were separated, and the aqueous layer was washed with Et_2O (5 mL x2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (10% Et_2O in hexanes), which furnished the product as a clear, colorless oil. First run: 46 mg (92%, 98% ee). Second run: 45 mg (90%, 98% ee).

(3) Hamman, S.; Michals, D. R.; Pickard, S. T.; Smith, H. E. *J. Fluorine Chem.* **1993**, *62*, 131–137.

The ee of the product was determined by chiral GC (CP-Chirasil-DEX CB; heating program: 105 °C → 115 °C @ 1 °C/min, followed by 115 → 175 °C @ 5 °C/min; He flow rate: 1.0 mL/min; retention times: 29.8 min (minor), 30.2 min (major)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.38 (m, 2H), 7.33–7.30 (m, 3H), 3.91–3.80 (m, 2H), 2.22–2.11 (m, 1H), 1.98–1.80 (m, 1H), 0.82 (t, 3H, J = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 128.4, 127.6, 124.8, 100.4 (d, J_{CF} = 176 Hz), 68.8, 28.9, 7.1.

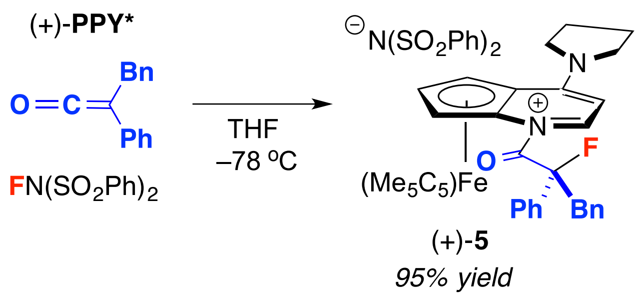
^{19}F NMR (282 MHz, $CDCl_3$) δ –170.5 (ddt, J = 22 Hz, J = 21 Hz, J = 45 Hz).

FT-IR (neat) 3400, 2918, 2360, 1497, 1448, 1061, 913, 878, 759 cm^{-1}.

$[\alpha]^{25}_D$ = –4.0 (c = 1.0, $CHCl_3$).

$[\alpha]^{25}_D$ = –2.2 (c = 1.0, MeOH).[4]

V. Synthesis of the Acylpyridinium Salt



Eq 4. NFSI (67.3 mg, 0.213 mmol; NFSI should be recrystallized from dichloromethane/*n*-hexanes before use) was added to an oven-dried 100-mL round-bottom flask equipped with a stir bar. The flask was capped with a rubber septum, and then it was evacuated and backfilled with nitrogen (three cycles); next, THF (47 mL) was added via syringe. (+)-**PPY*** (80.3 mg, 0.213 mmol) was added to an oven-dried 4-mL vial, and this vial was capped, and then it was evacuated and backfilled with nitrogen (three cycles); next, THF (1.0 mL) was added. Another 4-mL vial was evacuated and backfilled with nitrogen (three cycles); next, phenyl benzyl ketene (44.4 mg, 0.213 mmol) and THF (2.0 mL) were added in turn via syringe. A nitrogen balloon was attached to the flask that contained the NFSI solution, which was then cooled to –78 °C, and the solution of (+)-**PPY*** was added to the vial via syringe. Then, the solution of ketene was added dropwise to the vial via syringe pump over 20 min (color change: purple → violet → blue). The reaction mixture was stirred at –78 °C for an additional 30 min, and then it was concentrated under high vacuum (250 mtorr; the mixture was not exposed to the air) at r.t., furnishing acylpyridinium salt **5** as a blue solid (190 mg; ~90% pure by ^{1}H NMR spectroscopy; 95% yield by ^{1}H NMR spectroscopy vs. an internal standard). This salt is stable at r.t. for at least six months under N_2 atmosphere.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.07–8.00 (m, 1H), 7.80–7.74 (m, 5H), 7.60–7.40 (m, 5H), 7.34–7.16 (m, 10H), 6.13 (s, 1H), 5.83–5.73 (m, 1H), 4.63–4.51 (m, 1H), 4.43–4.34 (m, 1H), 3.90–3.78 (m, 4H), 3.75–3.51 (m, 2H), 2.25–2.04 (m, 4H), 1.54 (s, 15H).

^{19}F NMR (282 MHz, CD_2Cl_2) δ –159.6 (t, J = 26 Hz).

(4) Goj, O.; Burchardt, A.; Haufe, G. *Tetrahedron: Asymmetry* **1997**, *8*, 399–408.

FT-IR (neat) 3063, 2916, 1717, 1684, 1653, 1611, 1498, 1478, 1445, 1383, 1347, 1327, 1280, 1237, 1154, 1133, 1086, 1052, 998, 921, 790, 753, 720 cm^{-1}.

MS (FAB) *m/z* (M$^+$) calcd for $C_{37}H_{40}FFeN_2O$: 603, found: 603.

$[\alpha]^{25}_D$ = +1904 (c = 0.010, $CHCl_3$).

Anion exchange with cesium carborane. In a nitrogen-filled glovebox, acylpyridinium salt **5** (59.4 mg, 0.066 mmol) was dissolved in CH_2Cl_2 (1.5 mL). To this solution was added $Cs(CB_{11}H_{12})$ in CH_3CN (0.3 mL) at r.t., resulting in the formation of a white precipitate. After 30 min, the solution was filtered through an acrodisc to remove the precipitated $CsN(SO_2Ph)_2$, and then the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 (1.0 mL), and this solution was then filtered through an acrodisc to remove the remaining cesium salt. The solvent was removed, furnishing a blue solid. Crystals suitable for X-ray crystallography were grown from CH_2Cl_2/pentane at –20 °C.

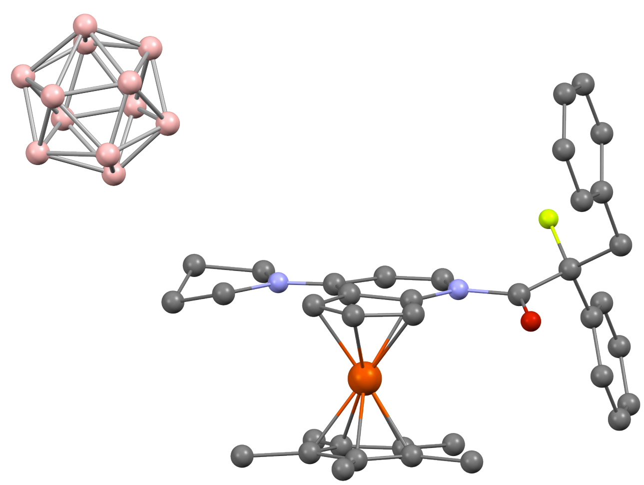
^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.05–8.00 (m, 1H), 7.56–7.49 (m, 5H), 7.23–7.20 (m, 3H), 7.12–7.09 (m, 2H), 6.00 (d, 1H, *J* = 3.5 Hz), 5.85–5.84 (m, 1H), 5.36 (s, 1H), 4.57–4.56 (m, 1H), 4.47–4.46 (m, 1H), 3.87–3.75 (m, 5H), 3.62 (dd, 1H, *J* = 14.5 Hz, *J* = 27.5 Hz), 2.37 (br s, 2H), 2.33–2.08 (m, 5H), 2.06–1.63 (m, 2H), 1.57 (s, 15H), 1.38–1.02 (m, 4H), 0.90 (m, 2H).

^{19}F NMR (282 MHz, CD_2Cl_2) δ –160.0 (t, *J* = 26 Hz).

^{11}B NMR (160 MHz, CD_2Cl_2) δ –7.13 (s), –13.2 (s), –16.0 (s).

FT-IR (neat) 3336, 3061, 2920, 2544, 1723, 1609, 1559, 1498, 1477, 1416, 1382, 1346, 1325, 1256, 1231, 1212, 1172, 1086, 1067, 1022, 999, 954, 921, 857, 786, 771 cm^{-1}.

MS (FAB) *m/z* (M$^+$) calcd for $C_{37}H_{40}FFeN_2O$: 603, found: 603.



Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker Kappa diffractometer coupled to a Apex II CCD detector with graphite monochromated Mo K_α radiation (λ = 0.71073 Å) for the structure of compound syl004. The structure was solved by direct methods using SHELXS [1] and refined against F^2 on all data by full-matrix least squares with SHELXL-2013 [2] using established refinement techniques [3]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). Unless otherwise noted, all disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3- distances and displacement parameters (standard uncertainty 0.01 Å^2) as well as rigid bond restraints (standard uncertainty 0.002 Å^2) for anisotropic displacement parameters.

Compound syl004 crystallizes in the orthorhombic space group $P2_12_12_1$ with two molecules in the asymmetric unit along with two $CB_{11}H_{12}$ cages, 1.3 molecules of pentane, and 0.7 molecules of dichloromethane. In both iron complexes, the pentamethylcyclopentadienyl ligand was disordered over two positions. The occupancies for the major component refined to 0.541(11) and 0.69(3) for the first and second molecule, respectively. For the second moleculen the iron was also disordered over two positions and was refined with the pentamethylcyclopentadienyl disorder. The carbonyl group in the second iron molecule was also modeled as a two part disorder where the occupancies for the two components refined to 0.508(10) and 0.492(10). The asymmetric unit contains two solvent accessible voids, one of which was modeled as a pentane molecule disordered over two positions and the second as a mixture of pentane and dichloromethane. The proximity of the two solvent positions was sufficiently close to treat them as a single disorder. The occupancy of the dichloromethane and one of the pentane molecules refined to 0.705(7) and the other two pentane positions refined to 0.295(7). The anisotropic displacement parameters for the carbon atoms (C1T, C2T, C3T, C4T, C5T) in the pentane molecule sharing a site with dichloromethane did not refine well and were constrained to be equivalent. The C-Cl distances in the dichloromethane were restrained to be equivalent. The 1,2- and 1,3- carbon-carbon distances in all pentane molecules were restrained to 1.54(2) Å and 2.52(4) Å, respectively. One of the $CB_{11}H_{12}$ cages was disordered over two positions with occupancies, 0.708(6) and 0.291(7) for the major and minor components, respectively. The position of the carbon atom in the both carborane cages is uncertain, and the position of the carbon atoms was determined by the shortest bond length, which is significantly longer than the typical C-B bond length. The carbon atom in the carborane cage is most likely disordered over multiple positions leading to the distorted bond lengths, which was not modeled.

[1] Sheldrick, G. M. *Acta Cryst.* **1990**, A46, 467–473.

[2] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112–122.

[3] Müller, P. *Crystallography Reviews* **2009**, *15*, 57–83.

Table 1. Crystal data and structure refinement for syl004.

Identification code	syl004	
Empirical formula	C41.59 H60.47 B11 Cl0.70 F Fe N2 O	
Formula weight	823.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 14.8695(15) Å	α= 90°.
	b = 15.973(2) Å	β= 90°.
	c = 37.274(4) Å	γ = 90°.
Volume	8853.2(17) $Å^3$	
Z	8	
Density (calculated)	1.235 Mg/m^3	
Absorption coefficient	0.423 mm^{-1}	
F(000)	3472	
Crystal size	0.400 x 0.250 x 0.200 mm^3	
Theta range for data collection	1.679 to 25.027°.	
Index ranges	-17<=h<=17, -19<=k<=14, -43<=l<=44	
Reflections collected	65941	
Independent reflections	15615 [R(int) = 0.0679]	
Completeness to theta = 25.242°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6284	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15615 / 3857 / 1586	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0610, wR2 = 0.1396	
R indices (all data)	R1 = 0.0960, wR2 = 0.1563	
Absolute structure parameter	-0.006(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.511 and -0.403 $e/Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2}x 10^3) for syl004. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	7238(1)	4901(1)	3584(1)	35(1)
C(1)	6922(8)	6144(8)	3519(4)	47(2)
C(2)	6989(9)	5771(8)	3181(3)	46(2)
C(3)	7871(8)	5445(9)	3143(3)	41(2)
C(4)	8352(8)	5606(13)	3467(4)	41(2)
C(5)	7770(9)	6062(9)	3701(4)	46(2)
C(6)	6119(9)	6586(10)	3670(5)	64(4)
C(7)	6271(10)	5761(11)	2887(5)	60(4)
C(8)	8246(12)	5058(11)	2805(3)	57(4)
C(9)	9337(9)	5420(20)	3524(6)	53(4)
C(10)	8014(13)	6397(13)	4064(4)	69(5)
C(1A)	6956(9)	6116(9)	3703(4)	48(2)
C(2A)	6817(9)	5959(11)	3332(4)	47(2)
C(3A)	7637(10)	5647(11)	3180(4)	42(2)
C(4A)	8306(9)	5652(15)	3459(5)	41(2)
C(5A)	7882(10)	5936(11)	3780(4)	44(2)
C(6A)	6284(11)	6487(12)	3958(6)	64(4)
C(7A)	5928(10)	6026(13)	3143(6)	61(4)
C(8A)	7788(13)	5333(12)	2810(4)	50(4)
C(9A)	9273(11)	5390(30)	3411(7)	51(5)
C(10A)	8329(15)	6097(15)	4139(5)	61(5)
C(11)	6964(4)	3695(4)	3437(1)	27(1)
C(12)	6160(4)	4102(4)	3543(2)	31(2)
C(13)	6276(4)	4362(5)	3901(2)	44(2)
C(14)	7141(4)	4149(5)	4020(2)	42(2)
C(15)	7597(4)	3714(4)	3729(2)	26(1)
C(16)	8488(4)	3395(4)	3683(2)	30(2)
N(2)	9119(3)	3446(4)	3932(1)	38(1)
C(19)	9016(4)	3871(6)	4280(2)	52(2)
C(20)	9962(4)	3948(6)	4426(2)	60(2)
C(21)	10436(5)	3221(5)	4261(2)	52(2)
C(22)	10043(4)	3107(5)	3882(2)	47(2)
C(17)	8668(4)	3028(4)	3340(2)	36(2)
C(18)	8044(4)	2978(4)	3081(2)	34(2)
N(1)	7181(3)	3280(3)	3114(1)	27(1)
C(23)	6546(4)	3257(5)	2835(2)	35(2)
O(1)	5919(3)	3739(3)	2834(1)	49(1)
C(24)	6662(4)	2650(5)	2523(2)	41(2)
F(1)	7106(2)	1932(2)	2651(1)	44(1)
C(25)	5730(5)	2345(5)	2393(2)	48(2)
C(26)	5230(5)	1851(6)	2669(2)	49(2)
C(27)	5407(6)	999(6)	2712(2)	56(2)
C(28)	4974(6)	524(7)	2969(2)	72(3)

C(29)	4327(6)	920(8)	3187(2)	72(3)
C(30)	4142(5)	1746(7)	3152(2)	63(3)
C(31)	4586(4)	2224(6)	2895(2)	51(2)
C(32)	7227(4)	3052(5)	2232(2)	40(2)
C(33)	7058(5)	3862(6)	2118(2)	58(2)
C(34)	7558(6)	4236(6)	1862(2)	66(2)
C(35)	8274(5)	3799(6)	1704(2)	57(2)
C(36)	8432(5)	2989(6)	1808(2)	60(2)
C(37)	7910(5)	2615(5)	2068(2)	50(2)
Fe(2)	3011(6)	4380(5)	5569(2)	31(1)
C(201)	1900(7)	5090(10)	5435(4)	38(2)
C(202)	2380(8)	4848(10)	5121(3)	40(2)
C(203)	3273(8)	5172(10)	5150(3)	41(2)
C(204)	3342(9)	5603(9)	5479(4)	41(2)
C(205)	2501(9)	5562(9)	5660(4)	38(2)
C(206)	937(8)	4896(14)	5516(5)	44(4)
C(207)	2038(10)	4342(12)	4809(3)	47(4)
C(208)	3981(10)	5083(14)	4865(4)	53(4)
C(209)	4171(11)	6049(12)	5608(6)	52(4)
C(210)	2265(13)	5956(11)	6015(4)	47(3)
C(211)	3312(4)	3833(4)	6039(2)	33(1)
C(212)	4085(4)	3913(5)	5827(2)	42(1)
C(213)	3908(4)	3482(5)	5504(2)	47(1)
C(214)	3038(5)	3145(5)	5505(2)	42(1)
C(215)	2636(4)	3366(4)	5846(2)	33(1)
C(216)	1769(4)	3233(4)	5996(2)	28(1)
N(202)	1099(4)	2852(4)	5834(1)	36(1)
C(219)	1122(5)	2520(5)	5463(2)	49(2)
C(220)	170(5)	2294(6)	5383(2)	64(2)
C(221)	-245(5)	2102(5)	5739(2)	54(2)
C(222)	213(4)	2704(5)	5994(2)	43(2)
C(217)	1644(4)	3569(4)	6352(2)	30(1)
C(218)	2298(4)	3976(4)	6530(2)	33(1)
N(201)	3146(3)	4114(3)	6396(1)	33(1)
C(223)	3893(17)	4512(16)	6569(6)	41(3)
O(201)	4570(11)	4695(10)	6417(5)	52(4)
C(224)	3749(17)	4786(16)	6946(6)	44(2)
F(201)	3210(30)	4222(17)	7141(12)	36(3)
C(225)	4532(14)	4941(17)	7174(7)	50(2)
C(226)	5090(20)	4121(16)	7146(8)	50(3)
C(227)	5685(15)	3961(14)	6869(6)	52(3)
C(228)	6129(14)	3204(14)	6866(5)	53(3)
C(229)	6013(14)	2612(15)	7121(6)	54(3)
C(230)	5385(16)	2755(17)	7396(6)	56(3)
C(231)	4920(30)	3500(20)	7407(10)	52(3)
C(232)	3386(14)	5644(12)	6956(5)	53(2)
C(233)	3805(14)	6313(11)	6785(4)	56(3)
C(234)	3429(15)	7121(12)	6791(5)	61(3)

C(235)	2612(18)	7219(16)	6986(7)	68(3)
C(236)	2218(17)	6619(13)	7134(5)	66(3)
C(237)	2621(16)	5805(12)	7142(5)	57(3)
Fe(2B)	2938(13)	4531(12)	5581(5)	38(2)
C(01B)	1806(15)	5215(19)	5508(7)	37(3)
C(02B)	2240(16)	5080(20)	5172(6)	40(3)
C(03B)	3138(17)	5399(19)	5195(6)	42(3)
C(04B)	3225(18)	5765(17)	5544(7)	40(3)
C(05B)	2409(17)	5673(17)	5735(7)	36(3)
C(06B)	836(16)	5060(30)	5597(10)	40(6)
C(07B)	1810(20)	4680(30)	4851(7)	51(6)
C(08B)	3840(20)	5450(30)	4902(8)	55(6)
C(09B)	4010(20)	6270(30)	5675(11)	44(6)
C(10B)	2190(30)	5960(30)	6111(8)	46(5)
C(23B)	3759(16)	4679(14)	6591(6)	40(3)
O(01B)	4322(10)	5023(10)	6415(5)	44(3)
C(24B)	3668(15)	4868(14)	6994(5)	44(2)
F(01B)	3250(30)	4166(19)	7151(13)	43(4)
C(25B)	4693(12)	4798(14)	7134(6)	48(2)
C(26B)	5082(19)	3934(15)	7173(8)	49(3)
C(27B)	5760(14)	3658(13)	6938(6)	54(3)
C(28B)	6166(13)	2896(13)	6976(6)	58(3)
C(29B)	5880(13)	2367(13)	7249(5)	56(3)
C(30B)	5226(16)	2602(15)	7484(6)	57(3)
C(31B)	4850(30)	3390(20)	7452(10)	51(3)
C(32B)	3044(12)	5622(10)	7030(5)	51(2)
C(33B)	3331(13)	6399(9)	6911(5)	59(3)
C(34B)	2869(15)	7125(13)	6919(6)	66(3)
C(35B)	1988(14)	7060(12)	7086(5)	70(3)
C(36B)	1672(13)	6307(10)	7209(4)	63(3)
C(37B)	2192(11)	5580(10)	7181(4)	50(2)
C(101)	2969(5)	4453(5)	3881(2)	53(2)
B(1)	2368(5)	3867(5)	3568(2)	40(2)
B(2)	1903(5)	4793(6)	3760(2)	46(2)
B(3)	2767(5)	5502(5)	3820(2)	42(2)
B(4)	3788(5)	5049(6)	3673(2)	45(2)
B(5)	3538(4)	4043(5)	3516(2)	34(2)
B(6)	2807(5)	4145(5)	3153(2)	39(2)
B(7)	1789(5)	4601(5)	3299(2)	44(2)
B(8)	2040(5)	5606(5)	3454(2)	40(2)
B(9)	3211(5)	5786(5)	3402(2)	41(2)
B(10)	3675(5)	4864(6)	3209(2)	43(2)
B(11)	2605(5)	5212(5)	3080(2)	41(2)
C(102)	2651(8)	9757(8)	4296(3)	73(2)
B(12)	1918(8)	9796(9)	4663(3)	67(2)
B(13)	3094(8)	10068(10)	4696(3)	69(2)
B(14)	3404(8)	10535(10)	4295(4)	72(2)
B(15)	2446(7)	10559(9)	4003(3)	65(2)

B(16)	1553(8)	10106(9)	4238(3)	62(2)
B(17)	1342(8)	10725(9)	4607(3)	62(2)
B(18)	2299(9)	10708(9)	4891(3)	66(2)
B(19)	3175(9)	11162(10)	4666(3)	70(2)
B(20)	2807(8)	11447(9)	4215(3)	66(2)
B(21)	1647(7)	11194(8)	4206(3)	54(2)
B(22)	2128(9)	11565(9)	4610(3)	65(2)
C(02A)	2178(15)	9584(14)	4315(5)	70(2)
B(12A)	2220(16)	9454(14)	4773(6)	70(2)
B(13A)	3209(14)	9651(15)	4520(7)	69(2)
B(14A)	2936(16)	10309(16)	4172(6)	70(2)
B(15A)	1768(15)	10583(17)	4203(6)	68(2)
B(16A)	1346(13)	10042(17)	4566(6)	67(2)
B(17A)	1874(15)	10398(16)	4948(5)	66(2)
B(18A)	3039(15)	10171(16)	4918(6)	68(2)
B(19A)	3459(13)	10723(16)	4554(7)	68(2)
B(20A)	2567(15)	11292(14)	4349(6)	67(2)
B(21A)	1608(15)	11113(16)	4621(6)	64(2)
B(22A)	2671(17)	11173(15)	4822(6)	66(2)
C(1S)	8995(13)	6889(12)	6237(4)	118(4)
Cl(1S)	9847(3)	6476(4)	6467(1)	109(2)
Cl(2S)	9254(5)	7254(6)	5829(2)	166(3)
C(1T)	9600(40)	6610(40)	6353(14)	133(4)
C(2T)	9220(30)	7350(30)	6159(10)	133(4)
C(3T)	9610(30)	7290(50)	5744(10)	133(4)
C(4T)	8710(20)	7470(30)	5548(10)	133(4)
C(5T)	8840(30)	7550(30)	5148(9)	133(4)
C(1U)	7592(15)	7489(12)	4936(5)	147(7)
C(2U)	7043(14)	7906(14)	5218(6)	170(5)
C(3U)	6024(14)	7852(16)	5188(6)	173(5)
C(4U)	5545(15)	8331(13)	5495(6)	158(5)
C(5U)	5715(13)	7863(12)	5861(5)	128(5)
C(1V)	6500(40)	7650(30)	4762(11)	150(8)
C(2V)	6250(50)	8010(30)	5141(11)	167(6)
C(3V)	6050(40)	7200(20)	5370(10)	167(6)
C(4V)	5960(40)	7470(30)	5774(10)	156(6)
C(5V)	5870(40)	8430(30)	5742(15)	155(9)

Table 3. Bond lengths [Å] and angles [°] for syl004.

Fe(1)-C(3A)	2.010(15)
Fe(1)-C(14)	2.025(7)
Fe(1)-C(2A)	2.033(14)
Fe(1)-C(1A)	2.035(14)
Fe(1)-C(15)	2.042(6)
Fe(1)-C(4A)	2.043(17)
Fe(1)-C(5A)	2.045(15)
Fe(1)-C(11)	2.045(6)
Fe(1)-C(13)	2.045(6)
Fe(1)-C(4)	2.049(15)
Fe(1)-C(12)	2.055(6)
Fe(1)-C(1)	2.055(13)
C(1)-C(2)	1.400(13)
C(1)-C(5)	1.438(13)
C(1)-C(6)	1.496(14)
C(2)-C(3)	1.418(13)
C(2)-C(7)	1.529(13)
C(3)-C(4)	1.428(14)
C(3)-C(8)	1.509(14)
C(4)-C(5)	1.428(14)
C(4)-C(9)	1.509(13)
C(5)-C(10)	1.499(14)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(1A)-C(2A)	1.422(14)
C(1A)-C(5A)	1.435(14)
C(1A)-C(6A)	1.502(15)
C(2A)-C(3A)	1.433(14)
C(2A)-C(7A)	1.502(14)
C(3A)-C(4A)	1.439(15)
C(3A)-C(8A)	1.486(15)
C(4A)-C(5A)	1.425(15)
C(4A)-C(9A)	1.508(15)

C(5A)-C(10A)	1.517(15)
C(6A)-H(6A1)	0.9800
C(6A)-H(6A2)	0.9800
C(6A)-H(6A3)	0.9800
C(7A)-H(7A1)	0.9800
C(7A)-H(7A2)	0.9800
C(7A)-H(7A3)	0.9800
C(8A)-H(8A1)	0.9800
C(8A)-H(8A2)	0.9800
C(8A)-H(8A3)	0.9800
C(9A)-H(9A1)	0.9800
C(9A)-H(9A2)	0.9800
C(9A)-H(9A3)	0.9800
C(10A)-H(10D)	0.9800
C(10A)-H(10E)	0.9800
C(10A)-H(10F)	0.9800
C(11)-N(1)	1.409(7)
C(11)-C(12)	1.417(8)
C(11)-C(15)	1.442(8)
C(12)-C(13)	1.407(9)
C(12)-H(12)	0.9500
C(13)-C(14)	1.403(9)
C(13)-H(13)	0.9500
C(14)-C(15)	1.454(8)
C(14)-H(14)	0.9500
C(15)-C(16)	1.430(8)
C(16)-N(2)	1.319(7)
C(16)-C(17)	1.432(9)
N(2)-C(19)	1.473(9)
N(2)-C(22)	1.489(8)
C(19)-C(20)	1.514(9)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.492(12)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-C(22)	1.541(9)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(17)-C(18)	1.342(8)
C(17)-H(17)	0.9500
C(18)-N(1)	1.378(8)
C(18)-H(18)	0.9500
N(1)-C(23)	1.406(7)
C(23)-O(1)	1.210(7)
C(23)-C(24)	1.524(9)

C(24)-F(1)	1.406(8)
C(24)-C(32)	1.516(9)
C(24)-C(25)	1.546(9)
C(25)-C(26)	1.494(10)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-C(27)	1.396(12)
C(26)-C(31)	1.407(10)
C(27)-C(28)	1.379(11)
C(27)-H(27)	0.9500
C(28)-C(29)	1.409(12)
C(28)-H(28)	0.9500
C(29)-C(30)	1.354(13)
C(29)-H(29)	0.9500
C(30)-C(31)	1.391(11)
C(30)-H(30)	0.9500
C(31)-H(31)	0.9500
C(32)-C(37)	1.376(9)
C(32)-C(33)	1.383(10)
C(33)-C(34)	1.351(10)
C(33)-H(33)	0.9500
C(34)-C(35)	1.403(11)
C(34)-H(34)	0.9500
C(35)-C(36)	1.371(12)
C(35)-H(35)	0.9500
C(36)-C(37)	1.376(10)
C(36)-H(36)	0.9500
C(37)-H(37)	0.9500
Fe(2)-C(213)	1.974(11)
Fe(2)-C(214)	1.988(11)
Fe(2)-C(215)	1.999(10)
Fe(2)-C(212)	2.009(10)
Fe(2)-C(211)	2.008(10)
Fe(2)-C(204)	2.042(11)
Fe(2)-C(203)	2.045(10)
Fe(2)-C(202)	2.055(9)
Fe(2)-C(205)	2.062(11)
Fe(2)-C(201)	2.064(10)
C(201)-C(202)	1.422(11)
C(201)-C(205)	1.440(11)
C(201)-C(206)	1.496(11)
C(202)-C(203)	1.428(11)
C(202)-C(207)	1.506(11)
C(203)-C(204)	1.409(11)
C(203)-C(208)	1.504(11)
C(204)-C(205)	1.424(11)
C(204)-C(209)	1.502(12)
C(205)-C(210)	1.506(11)

C(206)-H(20C)	0.9800
C(206)-H(20D)	0.9800
C(206)-H(20E)	0.9800
C(207)-H(20F)	0.9800
C(207)-H(20G)	0.9800
C(207)-H(20H)	0.9800
C(208)-H(20I)	0.9800
C(208)-H(20J)	0.9800
C(208)-H(20K)	0.9800
C(209)-H(20L)	0.9800
C(209)-H(20M)	0.9800
C(209)-H(20N)	0.9800
C(210)-H(21C)	0.9800
C(210)-H(21D)	0.9800
C(210)-H(21E)	0.9800
C(211)-C(212)	1.401(9)
C(211)-N(201)	1.426(7)
C(211)-C(215)	1.444(9)
C(212)-C(213)	1.413(10)
C(212)-H(212)	0.9500
C(213)-C(214)	1.401(10)
C(213)-H(213)	0.9500
C(214)-C(215)	1.445(8)
C(214)-H(214)	0.9500
C(215)-C(216)	1.422(8)
C(216)-N(202)	1.313(8)
C(216)-C(217)	1.444(8)
N(202)-C(222)	1.466(8)
N(202)-C(219)	1.481(8)
C(219)-C(220)	1.491(10)
C(219)-H(21F)	0.9900
C(219)-H(21G)	0.9900
C(220)-C(221)	1.492(10)
C(220)-H(22C)	0.9900
C(220)-H(22D)	0.9900
C(221)-C(222)	1.516(10)
C(221)-H(22E)	0.9900
C(221)-H(22F)	0.9900
C(222)-H(22G)	0.9900
C(222)-H(22H)	0.9900
C(217)-C(218)	1.344(8)
C(217)-H(217)	0.9500
C(218)-N(201)	1.374(8)
C(218)-H(218)	0.9500
N(201)-C(223)	1.43(3)
C(223)-O(201)	1.19(3)
C(223)-C(224)	1.49(3)
C(224)-F(201)	1.41(3)

C(224)-C(225)	1.46(3)
C(224)-C(232)	1.47(3)
C(225)-C(226)	1.56(3)
C(225)-H(22I)	0.9900
C(225)-H(22J)	0.9900
C(226)-C(227)	1.38(3)
C(226)-C(231)	1.41(3)
C(227)-C(228)	1.38(3)
C(227)-H(227)	0.9500
C(228)-C(229)	1.35(3)
C(228)-H(228)	0.9500
C(229)-C(230)	1.41(3)
C(229)-H(229)	0.9500
C(230)-C(231)	1.38(3)
C(230)-H(230)	0.9500
C(231)-H(231)	0.9500
C(232)-C(237)	1.36(3)
C(232)-C(233)	1.39(2)
C(233)-C(234)	1.41(3)
C(233)-H(233)	0.9500
C(234)-C(235)	1.42(3)
C(234)-H(234)	0.9500
C(235)-C(236)	1.25(3)
C(235)-H(235)	0.9500
C(236)-C(237)	1.43(3)
C(236)-H(236)	0.9500
C(237)-H(237)	0.9500
Fe(2B)-C(03B)	2.020(18)
Fe(2B)-C(04B)	2.021(18)
Fe(2B)-C(01B)	2.025(18)
Fe(2B)-C(02B)	2.042(17)
Fe(2B)-C(05B)	2.067(18)
C(01B)-C(02B)	1.424(16)
C(01B)-C(05B)	1.431(16)
C(01B)-C(06B)	1.500(16)
C(02B)-C(03B)	1.431(16)
C(02B)-C(07B)	1.501(16)
C(03B)-C(04B)	1.430(16)
C(03B)-C(08B)	1.516(16)
C(04B)-C(05B)	1.415(16)
C(04B)-C(09B)	1.502(17)
C(05B)-C(10B)	1.511(16)
C(06B)-H(06A)	0.9800
C(06B)-H(06B)	0.9800
C(06B)-H(06C)	0.9800
C(07B)-H(07A)	0.9800
C(07B)-H(07B)	0.9800
C(07B)-H(07C)	0.9800

C(08B)-H(08A)	0.9800
C(08B)-H(08B)	0.9800
C(08B)-H(08C)	0.9800
C(09B)-H(09A)	0.9800
C(09B)-H(09B)	0.9800
C(09B)-H(09C)	0.9800
C(10B)-H(10G)	0.9800
C(10B)-H(10H)	0.9800
C(10B)-H(10I)	0.9800
C(23B)-O(01B)	1.20(2)
C(23B)-C(24B)	1.54(2)
C(24B)-F(01B)	1.41(3)
C(24B)-C(32B)	1.53(2)
C(24B)-C(25B)	1.61(2)
C(25B)-C(26B)	1.50(2)
C(25B)-H(25C)	0.9900
C(25B)-H(25D)	0.9900
C(26B)-C(31B)	1.40(2)
C(26B)-C(27B)	1.41(2)
C(27B)-C(28B)	1.37(2)
C(27B)-H(27B)	0.9500
C(28B)-C(29B)	1.389(19)
C(28B)-H(28B)	0.9500
C(29B)-C(30B)	1.36(2)
C(29B)-H(29B)	0.9500
C(30B)-C(31B)	1.39(2)
C(30B)-H(30B)	0.9500
C(31B)-H(31B)	0.9500
C(32B)-C(33B)	1.385(19)
C(32B)-C(37B)	1.388(19)
C(33B)-C(34B)	1.35(2)
C(33B)-H(33B)	0.9500
C(34B)-C(35B)	1.45(2)
C(34B)-H(34B)	0.9500
C(35B)-C(36B)	1.37(2)
C(35B)-H(35B)	0.9500
C(36B)-C(37B)	1.398(18)
C(36B)-H(36B)	0.9500
C(37B)-H(37B)	0.9500
C(101)-B(3)	1.717(11)
C(101)-B(4)	1.730(10)
C(101)-B(5)	1.732(10)
C(101)-B(2)	1.734(10)
C(101)-B(1)	1.741(10)
C(101)-H(101)	0.9900
B(1)-B(6)	1.737(10)
B(1)-B(7)	1.768(11)
B(1)-B(5)	1.773(9)

B(1)-B(2)	1.782(11)
B(1)-H(1)	1.1200
B(2)-B(3)	1.727(12)
B(2)-B(8)	1.740(11)
B(2)-B(7)	1.752(11)
B(2)-H(2)	1.1200
B(3)-B(8)	1.747(10)
B(3)-B(9)	1.751(10)
B(3)-B(4)	1.769(10)
B(3)-H(3)	1.1200
B(4)-B(5)	1.751(12)
B(4)-B(10)	1.761(10)
B(4)-B(9)	1.772(11)
B(4)-H(4)	1.1200
B(5)-B(6)	1.741(9)
B(5)-B(10)	1.752(10)
B(5)-H(5)	1.1200
B(6)-B(10)	1.740(11)
B(6)-B(11)	1.752(11)
B(6)-B(7)	1.767(10)
B(6)-H(6)	1.1200
B(7)-B(8)	1.746(11)
B(7)-B(11)	1.759(11)
B(7)-H(7)	1.1200
B(8)-B(11)	1.747(10)
B(8)-B(9)	1.776(10)
B(8)-H(8)	1.1200
B(9)-B(11)	1.760(11)
B(9)-B(10)	1.779(11)
B(9)-H(9)	1.1200
B(10)-B(11)	1.752(10)
B(10)-H(10)	1.1200
B(11)-H(11)	1.1200
C(102)-B(14)	1.673(17)
C(102)-B(13)	1.704(16)
C(102)-B(15)	1.711(17)
C(102)-B(16)	1.740(15)
C(102)-B(12)	1.750(15)
C(102)-H(102)	0.9900
B(12)-B(17)	1.726(17)
B(12)-B(16)	1.746(16)
B(12)-B(18)	1.780(18)
B(12)-B(13)	1.807(16)
B(12)-H(12A)	1.1200
B(13)-B(18)	1.724(17)
B(13)-B(14)	1.734(17)
B(13)-B(19)	1.755(18)
B(13)-H(13A)	1.1200

B(14)-B(20)	1.732(17)
B(14)-B(19)	1.743(18)
B(14)-B(15)	1.793(15)
B(14)-H(14A)	1.1200
B(15)-B(20)	1.709(17)
B(15)-B(21)	1.735(15)
B(15)-B(16)	1.748(16)
B(15)-H(15)	1.1200
B(16)-B(17)	1.723(16)
B(16)-B(21)	1.747(17)
B(16)-H(16)	1.1200
B(17)-B(21)	1.733(16)
B(17)-B(18)	1.775(15)
B(17)-B(22)	1.780(17)
B(17)-H(17A)	1.1200
B(18)-B(19)	1.711(17)
B(18)-B(22)	1.744(16)
B(18)-H(18A)	1.1200
B(19)-B(22)	1.698(17)
B(19)-B(20)	1.827(15)
B(19)-H(19)	1.1200
B(20)-B(21)	1.772(16)
B(20)-B(22)	1.795(16)
B(20)-H(20)	1.1200
B(21)-B(22)	1.769(14)
B(21)-H(21)	1.1200
B(22)-H(22)	1.1200
C(02A)-B(14A)	1.70(2)
C(02A)-B(16A)	1.72(2)
C(02A)-B(13A)	1.72(2)
C(02A)-B(12A)	1.72(2)
C(02A)-B(15A)	1.76(2)
C(02A)-H(02A)	1.1200
B(12A)-B(17A)	1.72(2)
B(12A)-B(18A)	1.76(2)
B(12A)-B(13A)	1.78(2)
B(12A)-B(16A)	1.78(2)
B(12A)-H(12B)	1.1200
B(13A)-B(14A)	1.72(2)
B(13A)-B(18A)	1.72(2)
B(13A)-B(19A)	1.76(2)
B(13A)-H(13B)	1.1200
B(14A)-B(19A)	1.75(2)
B(14A)-B(20A)	1.79(2)
B(14A)-B(15A)	1.80(2)
B(14A)-H(14B)	1.1200
B(15A)-B(16A)	1.72(2)
B(15A)-B(20A)	1.73(2)

B(15A)-B(21A)	1.79(2)
B(15A)-H(15A)	1.1200
B(16A)-B(17A)	1.72(2)
B(16A)-B(21A)	1.77(2)
B(16A)-H(16A)	1.1200
B(17A)-B(21A)	1.72(2)
B(17A)-B(18A)	1.77(2)
B(17A)-B(22A)	1.78(2)
B(17A)-H(17B)	1.1200
B(18A)-B(22A)	1.73(2)
B(18A)-B(19A)	1.74(2)
B(18A)-H(18B)	1.1200
B(19A)-B(22A)	1.70(2)
B(19A)-B(20A)	1.78(2)
B(19A)-H(19C)	1.1200
B(20A)-B(21A)	1.77(2)
B(20A)-B(22A)	1.78(2)
B(20A)-H(20O)	1.1200
B(21A)-B(22A)	1.75(2)
B(21A)-H(21H)	1.1200
B(22A)-H(22K)	1.1200
C(1S)-Cl(1S)	1.667(16)
C(1S)-Cl(2S)	1.674(16)
C(1S)-H(1S1)	0.9900
C(1S)-H(1S2)	0.9900
C(1T)-C(2T)	1.50(3)
C(1T)-H(1T1)	0.9800
C(1T)-H(1T2)	0.9800
C(1T)-H(1T3)	0.9800
C(2T)-C(3T)	1.66(3)
C(2T)-H(2T1)	0.9900
C(2T)-H(2T2)	0.9900
C(3T)-C(4T)	1.55(3)
C(3T)-H(3T1)	0.9900
C(3T)-H(3T2)	0.9900
C(4T)-C(5T)	1.51(3)
C(4T)-H(4T1)	0.9900
C(4T)-H(4T2)	0.9900
C(5T)-H(5T1)	0.9800
C(5T)-H(5T2)	0.9800
C(5T)-H(5T3)	0.9800
C(1U)-C(2U)	1.488(18)
C(1U)-H(1U1)	0.9800
C(1U)-H(1U2)	0.9800
C(1U)-H(1U3)	0.9800
C(2U)-C(3U)	1.52(2)
C(2U)-H(2U1)	0.9900
C(2U)-H(2U2)	0.9900

C(3U)-C(4U)	1.55(2)
C(3U)-H(3U1)	0.9900
C(3U)-H(3U2)	0.9900
C(4U)-C(5U)	1.58(2)
C(4U)-H(4U1)	0.9900
C(4U)-H(4U2)	0.9900
C(5U)-H(5U1)	0.9800
C(5U)-H(5U2)	0.9800
C(5U)-H(5U3)	0.9800
C(1V)-C(2V)	1.57(3)
C(1V)-H(1V1)	0.9800
C(1V)-H(1V2)	0.9800
C(1V)-H(1V3)	0.9800
C(2V)-C(3V)	1.58(3)
C(2V)-H(2V1)	0.9900
C(2V)-H(2V2)	0.9900
C(3V)-C(4V)	1.57(3)
C(3V)-H(3V1)	0.9900
C(3V)-H(3V2)	0.9900
C(4V)-C(5V)	1.54(3)
C(4V)-H(4V1)	0.9900
C(4V)-H(4V2)	0.9900
C(5V)-H(5V1)	0.9800
C(5V)-H(5V2)	0.9800
C(5V)-H(5V3)	0.9800

C(3A)-Fe(1)-C(14)	166.8(5)
C(3A)-Fe(1)-C(2A)	41.5(5)
C(14)-Fe(1)-C(2A)	147.4(5)
C(3A)-Fe(1)-C(1A)	70.0(6)
C(14)-Fe(1)-C(1A)	112.1(5)
C(2A)-Fe(1)-C(1A)	40.9(4)
C(3A)-Fe(1)-C(15)	132.2(5)
C(14)-Fe(1)-C(15)	41.9(2)
C(2A)-Fe(1)-C(15)	167.1(5)
C(1A)-Fe(1)-C(15)	151.8(5)
C(3A)-Fe(1)-C(4A)	41.6(5)
C(14)-Fe(1)-C(4A)	125.9(6)
C(2A)-Fe(1)-C(4A)	69.2(7)
C(1A)-Fe(1)-C(4A)	69.5(7)
C(15)-Fe(1)-C(4A)	113.7(6)
C(3A)-Fe(1)-C(5A)	69.5(6)
C(14)-Fe(1)-C(5A)	103.1(5)
C(2A)-Fe(1)-C(5A)	68.7(6)
C(1A)-Fe(1)-C(5A)	41.2(5)
C(15)-Fe(1)-C(5A)	122.3(5)
C(4A)-Fe(1)-C(5A)	40.8(5)
C(3A)-Fe(1)-C(11)	114.6(5)

C(14)-Fe(1)-C(11)	69.1(2)
C(2A)-Fe(1)-C(11)	126.7(5)
C(1A)-Fe(1)-C(11)	156.4(4)
C(15)-Fe(1)-C(11)	41.3(2)
C(4A)-Fe(1)-C(11)	130.3(6)
C(5A)-Fe(1)-C(11)	162.0(5)
C(3A)-Fe(1)-C(13)	152.7(5)
C(14)-Fe(1)-C(13)	40.3(3)
C(2A)-Fe(1)-C(13)	113.7(5)
C(1A)-Fe(1)-C(13)	97.5(5)
C(15)-Fe(1)-C(13)	68.9(3)
C(4A)-Fe(1)-C(13)	157.2(5)
C(5A)-Fe(1)-C(13)	117.5(5)
C(11)-Fe(1)-C(13)	67.6(3)
C(14)-Fe(1)-C(4)	123.7(5)
C(15)-Fe(1)-C(4)	110.8(6)
C(11)-Fe(1)-C(4)	128.5(5)
C(13)-Fe(1)-C(4)	156.8(5)
C(3A)-Fe(1)-C(12)	122.9(5)
C(14)-Fe(1)-C(12)	68.6(3)
C(2A)-Fe(1)-C(12)	104.0(5)
C(1A)-Fe(1)-C(12)	116.6(4)
C(15)-Fe(1)-C(12)	69.3(2)
C(4A)-Fe(1)-C(12)	162.5(5)
C(5A)-Fe(1)-C(12)	153.4(5)
C(11)-Fe(1)-C(12)	40.4(2)
C(13)-Fe(1)-C(12)	40.2(2)
C(4)-Fe(1)-C(12)	162.9(5)
C(14)-Fe(1)-C(1)	130.6(5)
C(15)-Fe(1)-C(1)	171.1(5)
C(11)-Fe(1)-C(1)	146.4(4)
C(13)-Fe(1)-C(1)	108.3(5)
C(4)-Fe(1)-C(1)	68.2(6)
C(12)-Fe(1)-C(1)	114.4(4)
C(2)-C(1)-C(5)	108.9(9)
C(2)-C(1)-C(6)	126.6(12)
C(5)-C(1)-C(6)	124.4(12)
C(2)-C(1)-Fe(1)	71.2(7)
C(5)-C(1)-Fe(1)	69.9(7)
C(6)-C(1)-Fe(1)	126.5(11)
C(1)-C(2)-C(3)	108.1(9)
C(1)-C(2)-C(7)	126.9(12)
C(3)-C(2)-C(7)	124.8(12)
C(1)-C(2)-Fe(1)	69.2(7)
C(3)-C(2)-Fe(1)	70.2(7)
C(7)-C(2)-Fe(1)	129.4(10)
C(2)-C(3)-C(4)	108.3(10)
C(2)-C(3)-C(8)	125.1(11)

C(4)-C(3)-C(8)	126.5(11)
C(2)-C(3)-Fe(1)	70.0(7)
C(4)-C(3)-Fe(1)	68.5(7)
C(8)-C(3)-Fe(1)	130.9(10)
C(3)-C(4)-C(5)	107.8(10)
C(3)-C(4)-C(9)	124.8(13)
C(5)-C(4)-C(9)	127.0(14)
C(3)-C(4)-Fe(1)	71.1(7)
C(5)-C(4)-Fe(1)	70.2(8)
C(9)-C(4)-Fe(1)	130.3(17)
C(4)-C(5)-C(1)	106.8(10)
C(4)-C(5)-C(10)	125.9(12)
C(1)-C(5)-C(10)	127.3(12)
C(4)-C(5)-Fe(1)	69.2(8)
C(1)-C(5)-Fe(1)	69.3(7)
C(10)-C(5)-Fe(1)	127.2(12)
C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(4)-C(9)-H(9A)	109.5
C(4)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(4)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(2A)-C(1A)-C(5A)	107.3(10)
C(2A)-C(1A)-C(6A)	126.1(13)

C(5A)-C(1A)-C(6A)	126.2(13)
C(2A)-C(1A)-Fe(1)	69.5(8)
C(5A)-C(1A)-Fe(1)	69.8(8)
C(6A)-C(1A)-Fe(1)	130.7(13)
C(1A)-C(2A)-C(3A)	108.7(10)
C(1A)-C(2A)-C(7A)	124.9(14)
C(3A)-C(2A)-C(7A)	126.1(14)
C(1A)-C(2A)-Fe(1)	69.6(8)
C(3A)-C(2A)-Fe(1)	68.4(8)
C(7A)-C(2A)-Fe(1)	123.2(12)
C(2A)-C(3A)-C(4A)	107.5(11)
C(2A)-C(3A)-C(8A)	127.8(13)
C(4A)-C(3A)-C(8A)	124.7(13)
C(2A)-C(3A)-Fe(1)	70.1(8)
C(4A)-C(3A)-Fe(1)	70.5(9)
C(8A)-C(3A)-Fe(1)	122.7(12)
C(5A)-C(4A)-C(3A)	107.6(11)
C(5A)-C(4A)-C(9A)	127.5(15)
C(3A)-C(4A)-C(9A)	124.9(14)
C(5A)-C(4A)-Fe(1)	69.6(9)
C(3A)-C(4A)-Fe(1)	68.0(8)
C(9A)-C(4A)-Fe(1)	127(2)
C(4A)-C(5A)-C(1A)	108.7(11)
C(4A)-C(5A)-C(10A)	126.9(14)
C(1A)-C(5A)-C(10A)	124.2(13)
C(4A)-C(5A)-Fe(1)	69.5(9)
C(1A)-C(5A)-Fe(1)	69.0(8)
C(10A)-C(5A)-Fe(1)	131.1(14)
C(1A)-C(6A)-H(6A1)	109.5
C(1A)-C(6A)-H(6A2)	109.5
H(6A1)-C(6A)-H(6A2)	109.5
C(1A)-C(6A)-H(6A3)	109.5
H(6A1)-C(6A)-H(6A3)	109.5
H(6A2)-C(6A)-H(6A3)	109.5
C(2A)-C(7A)-H(7A1)	109.5
C(2A)-C(7A)-H(7A2)	109.5
H(7A1)-C(7A)-H(7A2)	109.5
C(2A)-C(7A)-H(7A3)	109.5
H(7A1)-C(7A)-H(7A3)	109.5
H(7A2)-C(7A)-H(7A3)	109.5
C(3A)-C(8A)-H(8A1)	109.5
C(3A)-C(8A)-H(8A2)	109.5
H(8A1)-C(8A)-H(8A2)	109.5
C(3A)-C(8A)-H(8A3)	109.5
H(8A1)-C(8A)-H(8A3)	109.5
H(8A2)-C(8A)-H(8A3)	109.5
C(4A)-C(9A)-H(9A1)	109.5
C(4A)-C(9A)-H(9A2)	109.5

H(9A1)-C(9A)-H(9A2)	109.5
C(4A)-C(9A)-H(9A3)	109.5
H(9A1)-C(9A)-H(9A3)	109.5
H(9A2)-C(9A)-H(9A3)	109.5
C(5A)-C(10A)-H(10D)	109.5
C(5A)-C(10A)-H(10E)	109.5
H(10D)-C(10A)-H(10E)	109.5
C(5A)-C(10A)-H(10F)	109.5
H(10D)-C(10A)-H(10F)	109.5
H(10E)-C(10A)-H(10F)	109.5
N(1)-C(11)-C(12)	130.4(5)
N(1)-C(11)-C(15)	120.4(5)
C(12)-C(11)-C(15)	109.1(5)
N(1)-C(11)-Fe(1)	128.8(4)
C(12)-C(11)-Fe(1)	70.2(4)
C(15)-C(11)-Fe(1)	69.2(3)
C(13)-C(12)-C(11)	107.4(5)
C(13)-C(12)-Fe(1)	69.6(4)
C(11)-C(12)-Fe(1)	69.4(3)
C(13)-C(12)-H(12)	126.3
C(11)-C(12)-H(12)	126.3
Fe(1)-C(12)-H(12)	126.3
C(14)-C(13)-C(12)	109.8(6)
C(14)-C(13)-Fe(1)	69.1(4)
C(12)-C(13)-Fe(1)	70.3(3)
C(14)-C(13)-H(13)	125.1
C(12)-C(13)-H(13)	125.1
Fe(1)-C(13)-H(13)	127.2
C(13)-C(14)-C(15)	108.0(5)
C(13)-C(14)-Fe(1)	70.6(4)
C(15)-C(14)-Fe(1)	69.7(3)
C(13)-C(14)-H(14)	126.0
C(15)-C(14)-H(14)	126.0
Fe(1)-C(14)-H(14)	125.3
C(16)-C(15)-C(11)	120.5(5)
C(16)-C(15)-C(14)	133.7(5)
C(11)-C(15)-C(14)	105.6(5)
C(16)-C(15)-Fe(1)	122.8(4)
C(11)-C(15)-Fe(1)	69.5(3)
C(14)-C(15)-Fe(1)	68.4(4)
N(2)-C(16)-C(15)	123.6(6)
N(2)-C(16)-C(17)	121.2(6)
C(15)-C(16)-C(17)	115.2(5)
C(16)-N(2)-C(19)	124.9(6)
C(16)-N(2)-C(22)	123.1(6)
C(19)-N(2)-C(22)	111.9(5)
N(2)-C(19)-C(20)	105.0(6)
N(2)-C(19)-H(19A)	110.8

C(20)-C(19)-H(19A)	110.8
N(2)-C(19)-H(19B)	110.8
C(20)-C(19)-H(19B)	110.8
H(19A)-C(19)-H(19B)	108.8
C(21)-C(20)-C(19)	103.1(7)
C(21)-C(20)-H(20A)	111.1
C(19)-C(20)-H(20A)	111.1
C(21)-C(20)-H(20B)	111.1
C(19)-C(20)-H(20B)	111.1
H(20A)-C(20)-H(20B)	109.1
C(20)-C(21)-C(22)	106.9(6)
C(20)-C(21)-H(21A)	110.3
C(22)-C(21)-H(21A)	110.3
C(20)-C(21)-H(21B)	110.3
C(22)-C(21)-H(21B)	110.3
H(21A)-C(21)-H(21B)	108.6
N(2)-C(22)-C(21)	101.1(6)
N(2)-C(22)-H(22A)	111.5
C(21)-C(22)-H(22A)	111.5
N(2)-C(22)-H(22B)	111.5
C(21)-C(22)-H(22B)	111.5
H(22A)-C(22)-H(22B)	109.4
C(18)-C(17)-C(16)	122.6(6)
C(18)-C(17)-H(17)	118.7
C(16)-C(17)-H(17)	118.7
C(17)-C(18)-N(1)	123.9(6)
C(17)-C(18)-H(18)	118.1
N(1)-C(18)-H(18)	118.1
C(18)-N(1)-C(23)	123.3(5)
C(18)-N(1)-C(11)	117.1(5)
C(23)-N(1)-C(11)	119.4(5)
O(1)-C(23)-N(1)	120.1(6)
O(1)-C(23)-C(24)	119.4(5)
N(1)-C(23)-C(24)	120.4(6)
F(1)-C(24)-C(32)	109.1(5)
F(1)-C(24)-C(23)	108.3(5)
C(32)-C(24)-C(23)	109.8(6)
F(1)-C(24)-C(25)	105.7(6)
C(32)-C(24)-C(25)	113.9(5)
C(23)-C(24)-C(25)	109.8(5)
C(26)-C(25)-C(24)	113.3(6)
C(26)-C(25)-H(25A)	108.9
C(24)-C(25)-H(25A)	108.9
C(26)-C(25)-H(25B)	108.9
C(24)-C(25)-H(25B)	108.9
H(25A)-C(25)-H(25B)	107.7
C(27)-C(26)-C(31)	118.1(8)
C(27)-C(26)-C(25)	120.1(7)

C(31)-C(26)-C(25)	121.8(8)
C(28)-C(27)-C(26)	121.9(8)
C(28)-C(27)-H(27)	119.0
C(26)-C(27)-H(27)	119.0
C(27)-C(28)-C(29)	118.1(10)
C(27)-C(28)-H(28)	121.0
C(29)-C(28)-H(28)	121.0
C(30)-C(29)-C(28)	121.4(9)
C(30)-C(29)-H(29)	119.3
C(28)-C(29)-H(29)	119.3
C(29)-C(30)-C(31)	120.3(8)
C(29)-C(30)-H(30)	119.9
C(31)-C(30)-H(30)	119.9
C(30)-C(31)-C(26)	120.2(9)
C(30)-C(31)-H(31)	119.9
C(26)-C(31)-H(31)	119.9
C(37)-C(32)-C(33)	118.2(7)
C(37)-C(32)-C(24)	120.8(7)
C(33)-C(32)-C(24)	121.0(6)
C(34)-C(33)-C(32)	122.0(8)
C(34)-C(33)-H(33)	119.0
C(32)-C(33)-H(33)	119.0
C(33)-C(34)-C(35)	119.7(8)
C(33)-C(34)-H(34)	120.2
C(35)-C(34)-H(34)	120.2
C(36)-C(35)-C(34)	118.6(8)
C(36)-C(35)-H(35)	120.7
C(34)-C(35)-H(35)	120.7
C(35)-C(36)-C(37)	120.9(8)
C(35)-C(36)-H(36)	119.6
C(37)-C(36)-H(36)	119.6
C(32)-C(37)-C(36)	120.6(7)
C(32)-C(37)-H(37)	119.7
C(36)-C(37)-H(37)	119.7
C(213)-Fe(2)-C(214)	41.4(3)
C(213)-Fe(2)-C(215)	70.3(4)
C(214)-Fe(2)-C(215)	42.5(3)
C(213)-Fe(2)-C(212)	41.5(3)
C(214)-Fe(2)-C(212)	70.9(4)
C(215)-Fe(2)-C(212)	70.9(4)
C(213)-Fe(2)-C(211)	68.9(4)
C(214)-Fe(2)-C(211)	70.6(4)
C(215)-Fe(2)-C(211)	42.2(3)
C(212)-Fe(2)-C(211)	40.8(3)
C(213)-Fe(2)-C(204)	120.8(5)
C(214)-Fe(2)-C(204)	157.6(5)
C(215)-Fe(2)-C(204)	158.0(5)
C(212)-Fe(2)-C(204)	104.0(5)

C(211)-Fe(2)-C(204)	120.4(5)
C(213)-Fe(2)-C(203)	103.1(5)
C(214)-Fe(2)-C(203)	121.2(5)
C(215)-Fe(2)-C(203)	161.3(5)
C(212)-Fe(2)-C(203)	116.3(5)
C(211)-Fe(2)-C(203)	153.1(5)
C(204)-Fe(2)-C(203)	40.3(3)
C(213)-Fe(2)-C(202)	118.2(5)
C(214)-Fe(2)-C(202)	105.9(5)
C(215)-Fe(2)-C(202)	125.9(5)
C(212)-Fe(2)-C(202)	152.5(5)
C(211)-Fe(2)-C(202)	165.6(5)
C(204)-Fe(2)-C(202)	68.2(4)
C(203)-Fe(2)-C(202)	40.8(3)
C(213)-Fe(2)-C(205)	159.1(5)
C(214)-Fe(2)-C(205)	159.3(5)
C(215)-Fe(2)-C(205)	123.7(5)
C(212)-Fe(2)-C(205)	123.6(5)
C(211)-Fe(2)-C(205)	109.7(5)
C(204)-Fe(2)-C(205)	40.6(3)
C(203)-Fe(2)-C(205)	68.3(4)
C(202)-Fe(2)-C(205)	68.5(4)
C(213)-Fe(2)-C(201)	155.4(5)
C(214)-Fe(2)-C(201)	122.1(5)
C(215)-Fe(2)-C(201)	110.3(5)
C(212)-Fe(2)-C(201)	163.0(5)
C(211)-Fe(2)-C(201)	129.0(5)
C(204)-Fe(2)-C(201)	68.2(4)
C(203)-Fe(2)-C(201)	68.2(4)
C(202)-Fe(2)-C(201)	40.4(3)
C(205)-Fe(2)-C(201)	40.8(3)
C(202)-C(201)-C(205)	108.1(7)
C(202)-C(201)-C(206)	126.2(9)
C(205)-C(201)-C(206)	125.7(9)
C(202)-C(201)-Fe(2)	69.5(5)
C(205)-C(201)-Fe(2)	69.5(6)
C(206)-C(201)-Fe(2)	127.1(10)
C(201)-C(202)-C(203)	107.8(7)
C(201)-C(202)-C(207)	127.6(8)
C(203)-C(202)-C(207)	124.6(8)
C(201)-C(202)-Fe(2)	70.1(5)
C(203)-C(202)-Fe(2)	69.2(5)
C(207)-C(202)-Fe(2)	125.9(9)
C(204)-C(203)-C(202)	108.1(7)
C(204)-C(203)-C(208)	127.6(9)
C(202)-C(203)-C(208)	124.2(9)
C(204)-C(203)-Fe(2)	69.7(6)
C(202)-C(203)-Fe(2)	70.0(5)

C(208)-C(203)-Fe(2)	128.0(9)
C(203)-C(204)-C(205)	109.0(8)
C(203)-C(204)-C(209)	124.7(9)
C(205)-C(204)-C(209)	126.3(9)
C(203)-C(204)-Fe(2)	70.0(6)
C(205)-C(204)-Fe(2)	70.5(6)
C(209)-C(204)-Fe(2)	126.8(10)
C(204)-C(205)-C(201)	107.0(7)
C(204)-C(205)-C(210)	127.0(9)
C(201)-C(205)-C(210)	126.0(9)
C(204)-C(205)-Fe(2)	68.9(6)
C(201)-C(205)-Fe(2)	69.6(6)
C(210)-C(205)-Fe(2)	127.8(9)
C(201)-C(206)-H(20C)	109.5
C(201)-C(206)-H(20D)	109.5
H(20C)-C(206)-H(20D)	109.5
C(201)-C(206)-H(20E)	109.5
H(20C)-C(206)-H(20E)	109.5
H(20D)-C(206)-H(20E)	109.5
C(202)-C(207)-H(20F)	109.5
C(202)-C(207)-H(20G)	109.5
H(20F)-C(207)-H(20G)	109.5
C(202)-C(207)-H(20H)	109.5
H(20F)-C(207)-H(20H)	109.5
H(20G)-C(207)-H(20H)	109.5
C(203)-C(208)-H(20I)	109.5
C(203)-C(208)-H(20J)	109.5
H(20I)-C(208)-H(20J)	109.5
C(203)-C(208)-H(20K)	109.5
H(20I)-C(208)-H(20K)	109.5
H(20J)-C(208)-H(20K)	109.5
C(204)-C(209)-H(20L)	109.5
C(204)-C(209)-H(20M)	109.5
H(20L)-C(209)-H(20M)	109.5
C(204)-C(209)-H(20N)	109.5
H(20L)-C(209)-H(20N)	109.5
H(20M)-C(209)-H(20N)	109.5
C(205)-C(210)-H(21C)	109.5
C(205)-C(210)-H(21D)	109.5
H(21C)-C(210)-H(21D)	109.5
C(205)-C(210)-H(21E)	109.5
H(21C)-C(210)-H(21E)	109.5
H(21D)-C(210)-H(21E)	109.5
C(212)-C(211)-N(201)	129.7(6)
C(212)-C(211)-C(215)	109.7(5)
N(201)-C(211)-C(215)	120.6(5)
C(212)-C(211)-Fe(2)	69.6(4)
N(201)-C(211)-Fe(2)	129.6(5)

C(215)-C(211)-Fe(2)	68.6(4)
C(211)-C(212)-C(213)	106.4(6)
C(211)-C(212)-Fe(2)	69.6(4)
C(213)-C(212)-Fe(2)	67.9(5)
C(211)-C(212)-H(212)	126.8
C(213)-C(212)-H(212)	126.8
Fe(2)-C(212)-H(212)	127.3
C(214)-C(213)-C(212)	110.8(6)
C(214)-C(213)-Fe(2)	69.8(5)
C(212)-C(213)-Fe(2)	70.5(5)
C(214)-C(213)-H(213)	124.6
C(212)-C(213)-H(213)	124.6
Fe(2)-C(213)-H(213)	126.7
C(213)-C(214)-C(215)	106.9(6)
C(213)-C(214)-Fe(2)	68.8(5)
C(215)-C(214)-Fe(2)	69.2(5)
C(213)-C(214)-H(214)	126.5
C(215)-C(214)-H(214)	126.5
Fe(2)-C(214)-H(214)	127.1
C(216)-C(215)-C(211)	120.8(5)
C(216)-C(215)-C(214)	133.1(6)
C(211)-C(215)-C(214)	106.1(5)
C(216)-C(215)-Fe(2)	125.2(5)
C(211)-C(215)-Fe(2)	69.2(4)
C(214)-C(215)-Fe(2)	68.3(5)
N(202)-C(216)-C(215)	125.2(5)
N(202)-C(216)-C(217)	119.8(5)
C(215)-C(216)-C(217)	115.0(5)
C(216)-N(202)-C(222)	124.7(5)
C(216)-N(202)-C(219)	125.2(6)
C(222)-N(202)-C(219)	110.1(5)
N(202)-C(219)-C(220)	104.5(6)
N(202)-C(219)-H(21F)	110.8
C(220)-C(219)-H(21F)	110.8
N(202)-C(219)-H(21G)	110.8
C(220)-C(219)-H(21G)	110.8
H(21F)-C(219)-H(21G)	108.9
C(219)-C(220)-C(221)	105.4(6)
C(219)-C(220)-H(22C)	110.7
C(221)-C(220)-H(22C)	110.7
C(219)-C(220)-H(22D)	110.7
C(221)-C(220)-H(22D)	110.7
H(22C)-C(220)-H(22D)	108.8
C(220)-C(221)-C(222)	104.0(6)
C(220)-C(221)-H(22E)	111.0
C(222)-C(221)-H(22E)	111.0
C(220)-C(221)-H(22F)	111.0
C(222)-C(221)-H(22F)	111.0

H(22E)-C(221)-H(22F)	109.0
N(202)-C(222)-C(221)	104.5(6)
N(202)-C(222)-H(22G)	110.9
C(221)-C(222)-H(22G)	110.9
N(202)-C(222)-H(22H)	110.9
C(221)-C(222)-H(22H)	110.9
H(22G)-C(222)-H(22H)	108.9
C(218)-C(217)-C(216)	122.7(6)
C(218)-C(217)-H(217)	118.6
C(216)-C(217)-H(217)	118.6
C(217)-C(218)-N(201)	124.2(5)
C(217)-C(218)-H(218)	117.9
N(201)-C(218)-H(218)	117.9
C(218)-N(201)-C(211)	116.5(5)
C(218)-N(201)-C(223)	128.3(10)
C(211)-N(201)-C(223)	115.2(10)
O(201)-C(223)-N(201)	123.3(19)
O(201)-C(223)-C(224)	120(2)
N(201)-C(223)-C(224)	116.3(19)
F(201)-C(224)-C(225)	105(3)
F(201)-C(224)-C(232)	112(2)
C(225)-C(224)-C(232)	96.8(19)
F(201)-C(224)-C(223)	112(2)
C(225)-C(224)-C(223)	119(2)
C(232)-C(224)-C(223)	110.5(18)
C(224)-C(225)-C(226)	104(2)
C(224)-C(225)-H(22I)	110.9
C(226)-C(225)-H(22I)	110.9
C(224)-C(225)-H(22J)	110.9
C(226)-C(225)-H(22J)	110.9
H(22I)-C(225)-H(22J)	108.9
C(227)-C(226)-C(231)	120(2)
C(227)-C(226)-C(225)	123.3(19)
C(231)-C(226)-C(225)	116(2)
C(228)-C(227)-C(226)	118.3(18)
C(228)-C(227)-H(227)	120.8
C(226)-C(227)-H(227)	120.8
C(229)-C(228)-C(227)	123.1(19)
C(229)-C(228)-H(228)	118.4
C(227)-C(228)-H(228)	118.4
C(228)-C(229)-C(230)	119.0(19)
C(228)-C(229)-H(229)	120.5
C(230)-C(229)-H(229)	120.5
C(231)-C(230)-C(229)	119.6(19)
C(231)-C(230)-H(230)	120.2
C(229)-C(230)-H(230)	120.2
C(230)-C(231)-C(226)	120(2)
C(230)-C(231)-H(231)	120.2

C(226)-C(231)-H(231)	120.2
C(237)-C(232)-C(233)	117.7(18)
C(237)-C(232)-C(224)	119.8(18)
C(233)-C(232)-C(224)	122.6(17)
C(232)-C(233)-C(234)	121.2(19)
C(232)-C(233)-H(233)	119.4
C(234)-C(233)-H(233)	119.4
C(233)-C(234)-C(235)	116.6(19)
C(233)-C(234)-H(234)	121.7
C(235)-C(234)-H(234)	121.7
C(236)-C(235)-C(234)	123(2)
C(236)-C(235)-H(235)	118.6
C(234)-C(235)-H(235)	118.6
C(235)-C(236)-C(237)	120(2)
C(235)-C(236)-H(236)	119.8
C(237)-C(236)-H(236)	119.8
C(232)-C(237)-C(236)	120.9(19)
C(232)-C(237)-H(237)	119.5
C(236)-C(237)-H(237)	119.5
C(03B)-Fe(2B)-C(04B)	41.4(6)
C(03B)-Fe(2B)-C(01B)	69.9(8)
C(04B)-Fe(2B)-C(01B)	68.9(8)
C(03B)-Fe(2B)-C(02B)	41.3(5)
C(04B)-Fe(2B)-C(02B)	68.7(8)
C(01B)-Fe(2B)-C(02B)	41.0(5)
C(03B)-Fe(2B)-C(05B)	69.3(7)
C(04B)-Fe(2B)-C(05B)	40.5(5)
C(01B)-Fe(2B)-C(05B)	40.9(5)
C(02B)-Fe(2B)-C(05B)	68.5(7)
C(02B)-C(01B)-C(05B)	108.2(13)
C(02B)-C(01B)-C(06B)	127.2(17)
C(05B)-C(01B)-C(06B)	123.7(17)
C(02B)-C(01B)-Fe(2B)	70.1(10)
C(05B)-C(01B)-Fe(2B)	71.1(10)
C(06B)-C(01B)-Fe(2B)	133(2)
C(01B)-C(02B)-C(03B)	108.5(12)
C(01B)-C(02B)-C(07B)	124.8(17)
C(03B)-C(02B)-C(07B)	126.7(17)
C(01B)-C(02B)-Fe(2B)	68.9(10)
C(03B)-C(02B)-Fe(2B)	68.6(9)
C(07B)-C(02B)-Fe(2B)	129.2(19)
C(04B)-C(03B)-C(02B)	106.5(12)
C(04B)-C(03B)-C(08B)	124.8(17)
C(02B)-C(03B)-C(08B)	128.4(17)
C(04B)-C(03B)-Fe(2B)	69.3(10)
C(02B)-C(03B)-Fe(2B)	70.2(10)
C(08B)-C(03B)-Fe(2B)	131(2)
C(05B)-C(04B)-C(03B)	109.7(13)

C(05B)-C(04B)-C(09B)	123.9(16)
C(03B)-C(04B)-C(09B)	125.9(17)
C(05B)-C(04B)-Fe(2B)	71.5(10)
C(03B)-C(04B)-Fe(2B)	69.2(10)
C(09B)-C(04B)-Fe(2B)	132(2)
C(04B)-C(05B)-C(01B)	107.1(12)
C(04B)-C(05B)-C(10B)	128.0(17)
C(01B)-C(05B)-C(10B)	124.9(17)
C(04B)-C(05B)-Fe(2B)	68.0(10)
C(01B)-C(05B)-Fe(2B)	67.9(10)
C(10B)-C(05B)-Fe(2B)	128(2)
C(01B)-C(06B)-H(06A)	109.5
C(01B)-C(06B)-H(06B)	109.5
H(06A)-C(06B)-H(06B)	109.5
C(01B)-C(06B)-H(06C)	109.5
H(06A)-C(06B)-H(06C)	109.5
H(06B)-C(06B)-H(06C)	109.5
C(02B)-C(07B)-H(07A)	109.5
C(02B)-C(07B)-H(07B)	109.5
H(07A)-C(07B)-H(07B)	109.5
C(02B)-C(07B)-H(07C)	109.5
H(07A)-C(07B)-H(07C)	109.5
H(07B)-C(07B)-H(07C)	109.5
C(03B)-C(08B)-H(08A)	109.5
C(03B)-C(08B)-H(08B)	109.5
H(08A)-C(08B)-H(08B)	109.5
C(03B)-C(08B)-H(08C)	109.5
H(08A)-C(08B)-H(08C)	109.5
H(08B)-C(08B)-H(08C)	109.5
C(04B)-C(09B)-H(09A)	109.5
C(04B)-C(09B)-H(09B)	109.5
H(09A)-C(09B)-H(09B)	109.5
C(04B)-C(09B)-H(09C)	109.5
H(09A)-C(09B)-H(09C)	109.5
H(09B)-C(09B)-H(09C)	109.5
C(05B)-C(10B)-H(10G)	109.5
C(05B)-C(10B)-H(10H)	109.5
H(10G)-C(10B)-H(10H)	109.5
C(05B)-C(10B)-H(10I)	109.5
H(10G)-C(10B)-H(10I)	109.5
H(10H)-C(10B)-H(10I)	109.5
O(01B)-C(23B)-C(24B)	120(2)
F(01B)-C(24B)-C(32B)	109(2)
F(01B)-C(24B)-C(23B)	107(2)
C(32B)-C(24B)-C(23B)	107.1(15)
F(01B)-C(24B)-C(25B)	103(2)
C(32B)-C(24B)-C(25B)	126.9(18)
C(23B)-C(24B)-C(25B)	102.7(16)

C(26B)-C(25B)-C(24B)	117.2(18)
C(26B)-C(25B)-H(25C)	108.0
C(24B)-C(25B)-H(25C)	108.0
C(26B)-C(25B)-H(25D)	108.0
C(24B)-C(25B)-H(25D)	108.0
H(25C)-C(25B)-H(25D)	107.2
C(31B)-C(26B)-C(27B)	116.6(16)
C(31B)-C(26B)-C(25B)	123(2)
C(27B)-C(26B)-C(25B)	120.3(17)
C(28B)-C(27B)-C(26B)	122.2(16)
C(28B)-C(27B)-H(27B)	118.9
C(26B)-C(27B)-H(27B)	118.9
C(27B)-C(28B)-C(29B)	118.8(17)
C(27B)-C(28B)-H(28B)	120.6
C(29B)-C(28B)-H(28B)	120.6
C(30B)-C(29B)-C(28B)	121.5(17)
C(30B)-C(29B)-H(29B)	119.2
C(28B)-C(29B)-H(29B)	119.2
C(29B)-C(30B)-C(31B)	119.0(17)
C(29B)-C(30B)-H(30B)	120.5
C(31B)-C(30B)-H(30B)	120.5
C(30B)-C(31B)-C(26B)	122(2)
C(30B)-C(31B)-H(31B)	119.1
C(26B)-C(31B)-H(31B)	119.1
C(33B)-C(32B)-C(37B)	117.1(16)
C(33B)-C(32B)-C(24B)	119.4(16)
C(37B)-C(32B)-C(24B)	123.6(15)
C(34B)-C(33B)-C(32B)	127.3(18)
C(34B)-C(33B)-H(33B)	116.3
C(32B)-C(33B)-H(33B)	116.3
C(33B)-C(34B)-C(35B)	114.0(19)
C(33B)-C(34B)-H(34B)	123.0
C(35B)-C(34B)-H(34B)	123.0
C(36B)-C(35B)-C(34B)	121.0(17)
C(36B)-C(35B)-H(35B)	119.5
C(34B)-C(35B)-H(35B)	119.5
C(35B)-C(36B)-C(37B)	121.0(17)
C(35B)-C(36B)-H(36B)	119.5
C(37B)-C(36B)-H(36B)	119.5
C(32B)-C(37B)-C(36B)	119.6(16)
C(32B)-C(37B)-H(37B)	120.2
C(36B)-C(37B)-H(37B)	120.2
B(3)-C(101)-B(4)	61.8(5)
B(3)-C(101)-B(5)	110.5(5)
B(4)-C(101)-B(5)	60.8(4)
B(3)-C(101)-B(2)	60.0(5)
B(4)-C(101)-B(2)	110.8(5)
B(5)-C(101)-B(2)	111.2(5)

B(3)-C(101)-B(1)	110.3(5)
B(4)-C(101)-B(1)	111.0(5)
B(5)-C(101)-B(1)	61.4(4)
B(2)-C(101)-B(1)	61.7(4)
B(3)-C(101)-H(101)	120.6
B(4)-C(101)-H(101)	119.9
B(5)-C(101)-H(101)	120.1
B(2)-C(101)-H(101)	120.1
B(1)-C(101)-H(101)	119.9
B(6)-B(1)-C(101)	105.4(5)
B(6)-B(1)-B(7)	60.5(4)
C(101)-B(1)-B(7)	105.8(6)
B(6)-B(1)-B(5)	59.5(4)
C(101)-B(1)-B(5)	59.1(4)
B(7)-B(1)-B(5)	108.1(5)
B(6)-B(1)-B(2)	106.9(6)
C(101)-B(1)-B(2)	58.9(4)
B(7)-B(1)-B(2)	59.2(4)
B(5)-B(1)-B(2)	107.1(6)
B(6)-B(1)-H(1)	122.5
C(101)-B(1)-H(1)	123.7
B(7)-B(1)-H(1)	122.0
B(5)-B(1)-H(1)	121.9
B(2)-B(1)-H(1)	122.5
B(3)-B(2)-C(101)	59.5(4)
B(3)-B(2)-B(8)	60.5(4)
C(101)-B(2)-B(8)	107.3(5)
B(3)-B(2)-B(7)	108.3(5)
C(101)-B(2)-B(7)	106.8(5)
B(8)-B(2)-B(7)	60.0(4)
B(3)-B(2)-B(1)	107.9(5)
C(101)-B(2)-B(1)	59.3(4)
B(8)-B(2)-B(1)	108.2(5)
B(7)-B(2)-B(1)	60.0(4)
B(3)-B(2)-H(2)	121.4
C(101)-B(2)-H(2)	122.8
B(8)-B(2)-H(2)	121.6
B(7)-B(2)-H(2)	121.9
B(1)-B(2)-H(2)	121.7
C(101)-B(3)-B(2)	60.4(4)
C(101)-B(3)-B(8)	107.7(6)
B(2)-B(3)-B(8)	60.1(4)
C(101)-B(3)-B(9)	107.7(5)
B(2)-B(3)-B(9)	109.6(5)
B(8)-B(3)-B(9)	61.0(4)
C(101)-B(3)-B(4)	59.5(4)
B(2)-B(3)-B(4)	109.3(6)
B(8)-B(3)-B(4)	109.2(5)

B(9)-B(3)-B(4)	60.5(4)
C(101)-B(3)-H(3)	122.4
B(2)-B(3)-H(3)	120.7
B(8)-B(3)-H(3)	121.3
B(9)-B(3)-H(3)	121.0
B(4)-B(3)-H(3)	121.1
C(101)-B(4)-B(5)	59.7(4)
C(101)-B(4)-B(10)	106.3(5)
B(5)-B(4)-B(10)	59.8(4)
C(101)-B(4)-B(3)	58.8(4)
B(5)-B(4)-B(3)	107.3(5)
B(10)-B(4)-B(3)	106.9(5)
C(101)-B(4)-B(9)	106.2(5)
B(5)-B(4)-B(9)	108.5(5)
B(10)-B(4)-B(9)	60.4(4)
B(3)-B(4)-B(9)	59.3(4)
C(101)-B(4)-H(4)	123.2
B(5)-B(4)-H(4)	121.5
B(10)-B(4)-H(4)	122.3
B(3)-B(4)-H(4)	122.7
B(9)-B(4)-H(4)	121.8
C(101)-B(5)-B(6)	105.6(5)
C(101)-B(5)-B(4)	59.5(4)
B(6)-B(5)-B(4)	107.8(5)
C(101)-B(5)-B(10)	106.6(5)
B(6)-B(5)-B(10)	59.8(4)
B(4)-B(5)-B(10)	60.4(4)
C(101)-B(5)-B(1)	59.5(4)
B(6)-B(5)-B(1)	59.3(4)
B(4)-B(5)-B(1)	108.5(5)
B(10)-B(5)-B(1)	107.8(5)
C(101)-B(5)-H(5)	123.3
B(6)-B(5)-H(5)	122.8
B(4)-B(5)-H(5)	121.2
B(10)-B(5)-H(5)	121.9
B(1)-B(5)-H(5)	121.6
B(1)-B(6)-B(10)	109.9(5)
B(1)-B(6)-B(5)	61.3(4)
B(10)-B(6)-B(5)	60.4(4)
B(1)-B(6)-B(11)	108.9(5)
B(10)-B(6)-B(11)	60.2(4)
B(5)-B(6)-B(11)	108.6(6)
B(1)-B(6)-B(7)	60.6(4)
B(10)-B(6)-B(7)	109.1(6)
B(5)-B(6)-B(7)	109.6(5)
B(11)-B(6)-B(7)	60.0(4)
B(1)-B(6)-H(6)	120.5
B(10)-B(6)-H(6)	120.9

B(5)-B(6)-H(6)	120.8
B(11)-B(6)-H(6)	121.7
B(7)-B(6)-H(6)	121.1
B(8)-B(7)-B(2)	59.6(4)
B(8)-B(7)-B(11)	59.8(4)
B(2)-B(7)-B(11)	107.0(5)
B(8)-B(7)-B(6)	107.3(5)
B(2)-B(7)-B(6)	106.9(5)
B(11)-B(7)-B(6)	59.6(4)
B(8)-B(7)-B(1)	108.6(5)
B(2)-B(7)-B(1)	60.8(5)
B(11)-B(7)-B(1)	107.2(5)
B(6)-B(7)-B(1)	58.9(4)
B(8)-B(7)-H(7)	121.6
B(2)-B(7)-H(7)	122.1
B(11)-B(7)-H(7)	122.4
B(6)-B(7)-H(7)	122.7
B(1)-B(7)-H(7)	121.6
B(2)-B(8)-B(7)	60.4(5)
B(2)-B(8)-B(3)	59.4(4)
B(7)-B(8)-B(3)	107.6(6)
B(2)-B(8)-B(11)	108.1(6)
B(7)-B(8)-B(11)	60.5(4)
B(3)-B(8)-B(11)	106.9(5)
B(2)-B(8)-B(9)	107.9(5)
B(7)-B(8)-B(9)	108.8(6)
B(3)-B(8)-B(9)	59.6(4)
B(11)-B(8)-B(9)	59.9(4)
B(2)-B(8)-H(8)	121.8
B(7)-B(8)-H(8)	121.1
B(3)-B(8)-H(8)	122.7
B(11)-B(8)-H(8)	121.9
B(9)-B(8)-H(8)	121.5
B(3)-B(9)-B(11)	106.2(5)
B(3)-B(9)-B(4)	60.3(4)
B(11)-B(9)-B(4)	106.8(6)
B(3)-B(9)-B(8)	59.4(4)
B(11)-B(9)-B(8)	59.2(4)
B(4)-B(9)-B(8)	107.8(5)
B(3)-B(9)-B(10)	106.9(6)
B(11)-B(9)-B(10)	59.4(4)
B(4)-B(9)-B(10)	59.5(4)
B(8)-B(9)-B(10)	106.9(6)
B(3)-B(9)-H(9)	122.4
B(11)-B(9)-H(9)	122.9
B(4)-B(9)-H(9)	121.8
B(8)-B(9)-H(9)	122.2
B(10)-B(9)-H(9)	122.5

B(6)-B(10)-B(5)	59.8(4)
B(6)-B(10)-B(11)	60.2(4)
B(5)-B(10)-B(11)	108.1(5)
B(6)-B(10)-B(4)	107.4(5)
B(5)-B(10)-B(4)	59.8(4)
B(11)-B(10)-B(4)	107.7(5)
B(6)-B(10)-B(9)	107.9(5)
B(5)-B(10)-B(9)	108.1(5)
B(11)-B(10)-B(9)	59.8(4)
B(4)-B(10)-B(9)	60.1(4)
B(6)-B(10)-H(10)	121.9
B(5)-B(10)-H(10)	121.7
B(11)-B(10)-H(10)	121.7
B(4)-B(10)-H(10)	122.1
B(9)-B(10)-H(10)	121.7
B(8)-B(11)-B(6)	108.0(5)
B(8)-B(11)-B(10)	109.4(5)
B(6)-B(11)-B(10)	59.5(4)
B(8)-B(11)-B(7)	59.7(4)
B(6)-B(11)-B(7)	60.4(4)
B(10)-B(11)-B(7)	108.8(5)
B(8)-B(11)-B(9)	60.9(4)
B(6)-B(11)-B(9)	108.2(5)
B(10)-B(11)-B(9)	60.9(4)
B(7)-B(11)-B(9)	109.0(5)
B(8)-B(11)-H(11)	121.3
B(6)-B(11)-H(11)	122.0
B(10)-B(11)-H(11)	121.0
B(7)-B(11)-H(11)	121.3
B(9)-B(11)-H(11)	120.9
B(14)-C(102)-B(13)	61.8(7)
B(14)-C(102)-B(15)	64.0(7)
B(13)-C(102)-B(15)	114.2(9)
B(14)-C(102)-B(16)	113.0(9)
B(13)-C(102)-B(16)	112.2(9)
B(15)-C(102)-B(16)	60.9(7)
B(14)-C(102)-B(12)	113.2(9)
B(13)-C(102)-B(12)	63.1(7)
B(15)-C(102)-B(12)	111.2(8)
B(16)-C(102)-B(12)	60.0(7)
B(14)-C(102)-H(102)	117.8
B(13)-C(102)-H(102)	118.1
B(15)-C(102)-H(102)	118.6
B(16)-C(102)-H(102)	120.3
B(12)-C(102)-H(102)	119.7
B(17)-B(12)-B(16)	59.5(7)
B(17)-B(12)-C(102)	104.2(9)
B(16)-B(12)-C(102)	59.7(6)

B(17)-B(12)-B(18)	60.8(7)
B(16)-B(12)-B(18)	107.5(9)
C(102)-B(12)-B(18)	101.8(9)
B(17)-B(12)-B(13)	106.4(9)
B(16)-B(12)-B(13)	107.2(9)
C(102)-B(12)-B(13)	57.2(7)
B(18)-B(12)-B(13)	57.5(7)
B(17)-B(12)-H(12A)	122.4
B(16)-B(12)-H(12A)	121.1
C(102)-B(12)-H(12A)	125.6
B(18)-B(12)-H(12A)	123.7
B(13)-B(12)-H(12A)	123.3
C(102)-B(13)-B(18)	106.1(8)
C(102)-B(13)-B(14)	58.2(7)
B(18)-B(13)-B(14)	107.0(9)
C(102)-B(13)-B(19)	105.2(9)
B(18)-B(13)-B(19)	58.9(8)
B(14)-B(13)-B(19)	60.0(7)
C(102)-B(13)-B(12)	59.7(7)
B(18)-B(13)-B(12)	60.5(7)
B(14)-B(13)-B(12)	107.6(8)
B(19)-B(13)-B(12)	107.6(9)
C(102)-B(13)-H(13A)	123.8
B(18)-B(13)-H(13A)	122.4
B(14)-B(13)-H(13A)	122.3
B(19)-B(13)-H(13A)	122.8
B(12)-B(13)-H(13A)	121.2
C(102)-B(14)-B(20)	106.4(9)
C(102)-B(14)-B(13)	60.0(7)
B(20)-B(14)-B(13)	111.9(9)
C(102)-B(14)-B(19)	107.1(9)
B(20)-B(14)-B(19)	63.4(7)
B(13)-B(14)-B(19)	60.6(7)
C(102)-B(14)-B(15)	59.1(7)
B(20)-B(14)-B(15)	58.0(7)
B(13)-B(14)-B(15)	108.7(9)
B(19)-B(14)-B(15)	108.3(8)
C(102)-B(14)-H(14A)	123.5
B(20)-B(14)-H(14A)	120.5
B(13)-B(14)-H(14A)	119.8
B(19)-B(14)-H(14A)	120.7
B(15)-B(14)-H(14A)	122.7
B(20)-B(15)-C(102)	105.7(8)
B(20)-B(15)-B(21)	61.9(7)
C(102)-B(15)-B(21)	106.3(8)
B(20)-B(15)-B(16)	110.5(9)
C(102)-B(15)-B(16)	60.4(7)
B(21)-B(15)-B(16)	60.2(7)

B(20)-B(15)-B(14)	59.2(7)
C(102)-B(15)-B(14)	57.0(7)
B(21)-B(15)-B(14)	107.0(8)
B(16)-B(15)-B(14)	106.9(8)
B(20)-B(15)-H(15)	120.8
C(102)-B(15)-H(15)	124.0
B(21)-B(15)-H(15)	121.6
B(16)-B(15)-H(15)	120.5
B(14)-B(15)-H(15)	123.7
B(17)-B(16)-C(102)	104.8(8)
B(17)-B(16)-B(12)	59.7(7)
C(102)-B(16)-B(12)	60.3(6)
B(17)-B(16)-B(21)	59.9(7)
C(102)-B(16)-B(21)	104.6(9)
B(12)-B(16)-B(21)	108.6(9)
B(17)-B(16)-B(15)	107.5(9)
C(102)-B(16)-B(15)	58.8(7)
B(12)-B(16)-B(15)	109.6(8)
B(21)-B(16)-B(15)	59.5(7)
B(17)-B(16)-H(16)	122.9
C(102)-B(16)-H(16)	124.4
B(12)-B(16)-H(16)	120.3
B(21)-B(16)-H(16)	122.6
B(15)-B(16)-H(16)	121.4
B(16)-B(17)-B(12)	60.8(7)
B(16)-B(17)-B(21)	60.7(7)
B(12)-B(17)-B(21)	110.2(9)
B(16)-B(17)-B(18)	108.8(8)
B(12)-B(17)-B(18)	61.1(7)
B(21)-B(17)-B(18)	108.2(8)
B(16)-B(17)-B(22)	108.5(9)
B(12)-B(17)-B(22)	108.8(8)
B(21)-B(17)-B(22)	60.5(6)
B(18)-B(17)-B(22)	58.8(7)
B(16)-B(17)-H(17A)	121.1
B(12)-B(17)-H(17A)	120.2
B(21)-B(17)-H(17A)	120.7
B(18)-B(17)-H(17A)	121.9
B(22)-B(17)-H(17A)	122.0
B(19)-B(18)-B(13)	61.4(7)
B(19)-B(18)-B(22)	58.9(7)
B(13)-B(18)-B(22)	108.1(9)
B(19)-B(18)-B(17)	108.1(8)
B(13)-B(18)-B(17)	107.9(9)
B(22)-B(18)-B(17)	60.7(7)
B(19)-B(18)-B(12)	110.8(9)
B(13)-B(18)-B(12)	62.0(7)
B(22)-B(18)-B(12)	107.9(8)

B(17)-B(18)-B(12)	58.1(7)
B(19)-B(18)-H(18A)	120.7
B(13)-B(18)-H(18A)	120.7
B(22)-B(18)-H(18A)	122.2
B(17)-B(18)-H(18A)	122.5
B(12)-B(18)-H(18A)	120.8
B(22)-B(19)-B(18)	61.5(7)
B(22)-B(19)-B(14)	107.4(8)
B(18)-B(19)-B(14)	107.2(10)
B(22)-B(19)-B(13)	108.8(9)
B(18)-B(19)-B(13)	59.7(7)
B(14)-B(19)-B(13)	59.4(8)
B(22)-B(19)-B(20)	61.1(6)
B(18)-B(19)-B(20)	109.2(8)
B(14)-B(19)-B(20)	58.0(7)
B(13)-B(19)-B(20)	106.6(9)
B(22)-B(19)-H(19)	120.5
B(18)-B(19)-H(19)	121.0
B(14)-B(19)-H(19)	123.2
B(13)-B(19)-H(19)	122.2
B(20)-B(19)-H(19)	122.0
B(15)-B(20)-B(14)	62.8(7)
B(15)-B(20)-B(21)	59.8(7)
B(14)-B(20)-B(21)	108.1(9)
B(15)-B(20)-B(22)	106.8(9)
B(14)-B(20)-B(22)	103.6(9)
B(21)-B(20)-B(22)	59.5(6)
B(15)-B(20)-B(19)	108.2(9)
B(14)-B(20)-B(19)	58.6(7)
B(21)-B(20)-B(19)	104.6(9)
B(22)-B(20)-B(19)	55.9(6)
B(15)-B(20)-H(20)	120.2
B(14)-B(20)-H(20)	122.0
B(21)-B(20)-H(20)	122.4
B(22)-B(20)-H(20)	124.8
B(19)-B(20)-H(20)	124.2
B(17)-B(21)-B(15)	107.6(9)
B(17)-B(21)-B(16)	59.3(7)
B(15)-B(21)-B(16)	60.3(7)
B(17)-B(21)-B(22)	61.1(7)
B(15)-B(21)-B(22)	106.8(8)
B(16)-B(21)-B(22)	107.9(8)
B(17)-B(21)-B(20)	109.7(8)
B(15)-B(21)-B(20)	58.3(7)
B(16)-B(21)-B(20)	107.7(9)
B(22)-B(21)-B(20)	60.9(6)
B(17)-B(21)-H(21)	121.0
B(15)-B(21)-H(21)	122.9

B(16)-B(21)-H(21)	122.0
B(22)-B(21)-H(21)	121.5
B(20)-B(21)-H(21)	121.4
B(19)-B(22)-B(18)	59.6(7)
B(19)-B(22)-B(21)	110.5(9)
B(18)-B(22)-B(21)	108.0(9)
B(19)-B(22)-B(17)	108.5(9)
B(18)-B(22)-B(17)	60.5(7)
B(21)-B(22)-B(17)	58.5(6)
B(19)-B(22)-B(20)	63.0(7)
B(18)-B(22)-B(20)	109.2(9)
B(21)-B(22)-B(20)	59.6(6)
B(17)-B(22)-B(20)	106.6(8)
B(19)-B(22)-H(22)	119.8
B(18)-B(22)-H(22)	121.5
B(21)-B(22)-H(22)	121.8
B(17)-B(22)-H(22)	122.9
B(20)-B(22)-H(22)	121.1
B(14A)-C(02A)-B(16A)	111.0(13)
B(14A)-C(02A)-B(13A)	60.3(10)
B(16A)-C(02A)-B(13A)	112.0(12)
B(14A)-C(02A)-B(12A)	111.7(13)
B(16A)-C(02A)-B(12A)	62.4(10)
B(13A)-C(02A)-B(12A)	62.2(10)
B(14A)-C(02A)-B(15A)	62.5(10)
B(16A)-C(02A)-B(15A)	59.5(10)
B(13A)-C(02A)-B(15A)	111.0(13)
B(12A)-C(02A)-B(15A)	110.9(13)
B(14A)-C(02A)-H(02A)	119.7
B(16A)-C(02A)-H(02A)	119.9
B(13A)-C(02A)-H(02A)	119.7
B(12A)-C(02A)-H(02A)	119.0
B(15A)-C(02A)-H(02A)	120.4
C(02A)-B(12A)-B(17A)	105.0(13)
C(02A)-B(12A)-B(18A)	104.6(13)
B(17A)-B(12A)-B(18A)	61.3(10)
C(02A)-B(12A)-B(13A)	58.8(10)
B(17A)-B(12A)-B(13A)	107.0(13)
B(18A)-B(12A)-B(13A)	58.3(10)
C(02A)-B(12A)-B(16A)	58.7(10)
B(17A)-B(12A)-B(16A)	58.9(10)
B(18A)-B(12A)-B(16A)	107.2(13)
B(13A)-B(12A)-B(16A)	106.4(12)
C(02A)-B(12A)-H(12B)	124.2
B(17A)-B(12A)-H(12B)	122.2
B(18A)-B(12A)-H(12B)	122.5
B(13A)-B(12A)-H(12B)	122.8
B(16A)-B(12A)-H(12B)	122.5

C(02A)-B(13A)-B(14A)	59.4(10)
C(02A)-B(13A)-B(18A)	106.4(12)
B(14A)-B(13A)-B(18A)	108.7(13)
C(02A)-B(13A)-B(19A)	106.4(12)
B(14A)-B(13A)-B(19A)	60.5(10)
B(18A)-B(13A)-B(19A)	59.9(10)
C(02A)-B(13A)-B(12A)	59.0(9)
B(14A)-B(13A)-B(12A)	108.3(12)
B(18A)-B(13A)-B(12A)	60.4(10)
B(19A)-B(13A)-B(12A)	108.1(13)
C(02A)-B(13A)-H(13B)	123.5
B(14A)-B(13A)-H(13B)	121.1
B(18A)-B(13A)-H(13B)	121.7
B(19A)-B(13A)-H(13B)	122.0
B(12A)-B(13A)-H(13B)	121.6
C(02A)-B(14A)-B(13A)	60.3(10)
C(02A)-B(14A)-B(19A)	107.3(12)
B(13A)-B(14A)-B(19A)	60.8(10)
C(02A)-B(14A)-B(20A)	106.2(12)
B(13A)-B(14A)-B(20A)	109.4(13)
B(19A)-B(14A)-B(20A)	60.4(10)
C(02A)-B(14A)-B(15A)	60.3(10)
B(13A)-B(14A)-B(15A)	109.2(13)
B(19A)-B(14A)-B(15A)	106.6(12)
B(20A)-B(14A)-B(15A)	57.7(9)
C(02A)-B(14A)-H(14B)	122.4
B(13A)-B(14A)-H(14B)	120.0
B(19A)-B(14A)-H(14B)	122.0
B(20A)-B(14A)-H(14B)	122.5
B(15A)-B(14A)-H(14B)	122.4
B(16A)-B(15A)-B(20A)	109.4(13)
B(16A)-B(15A)-C(02A)	59.0(10)
B(20A)-B(15A)-C(02A)	106.4(12)
B(16A)-B(15A)-B(21A)	60.4(10)
B(20A)-B(15A)-B(21A)	60.5(10)
C(02A)-B(15A)-B(21A)	105.6(12)
B(16A)-B(15A)-B(14A)	106.3(12)
B(20A)-B(15A)-B(14A)	61.0(10)
C(02A)-B(15A)-B(14A)	57.2(9)
B(21A)-B(15A)-B(14A)	107.5(12)
B(16A)-B(15A)-H(15A)	121.5
B(20A)-B(15A)-H(15A)	120.7
C(02A)-B(15A)-H(15A)	124.3
B(21A)-B(15A)-H(15A)	122.0
B(14A)-B(15A)-H(15A)	122.8
C(02A)-B(16A)-B(17A)	105.2(12)
C(02A)-B(16A)-B(15A)	61.5(10)
B(17A)-B(16A)-B(15A)	108.4(13)

C(02A)-B(16A)-B(21A)	108.5(13)
B(17A)-B(16A)-B(21A)	59.0(10)
B(15A)-B(16A)-B(21A)	61.6(10)
C(02A)-B(16A)-B(12A)	58.9(9)
B(17A)-B(16A)-B(12A)	58.9(10)
B(15A)-B(16A)-B(12A)	109.8(12)
B(21A)-B(16A)-B(12A)	107.5(12)
C(02A)-B(16A)-H(16A)	122.5
B(17A)-B(16A)-H(16A)	123.5
B(15A)-B(16A)-H(16A)	119.5
B(21A)-B(16A)-H(16A)	121.5
B(12A)-B(16A)-H(16A)	121.9
B(21A)-B(17A)-B(16A)	61.9(10)
B(21A)-B(17A)-B(12A)	112.5(13)
B(16A)-B(17A)-B(12A)	62.2(10)
B(21A)-B(17A)-B(18A)	108.5(12)
B(16A)-B(17A)-B(18A)	109.1(13)
B(12A)-B(17A)-B(18A)	60.4(10)
B(21A)-B(17A)-B(22A)	60.2(10)
B(16A)-B(17A)-B(22A)	108.5(13)
B(12A)-B(17A)-B(22A)	108.2(13)
B(18A)-B(17A)-B(22A)	58.3(9)
B(21A)-B(17A)-H(17B)	119.6
B(16A)-B(17A)-H(17B)	120.2
B(12A)-B(17A)-H(17B)	119.5
B(18A)-B(17A)-H(17B)	122.4
B(22A)-B(17A)-H(17B)	122.9
B(13A)-B(18A)-B(22A)	108.3(13)
B(13A)-B(18A)-B(19A)	61.1(10)
B(22A)-B(18A)-B(19A)	58.7(10)
B(13A)-B(18A)-B(12A)	61.4(10)
B(22A)-B(18A)-B(12A)	108.7(13)
B(19A)-B(18A)-B(12A)	109.8(13)
B(13A)-B(18A)-B(17A)	107.2(12)
B(22A)-B(18A)-B(17A)	61.0(10)
B(19A)-B(18A)-B(17A)	107.2(12)
B(12A)-B(18A)-B(17A)	58.4(10)
B(13A)-B(18A)-H(18B)	121.1
B(22A)-B(18A)-H(18B)	121.5
B(19A)-B(18A)-H(18B)	121.5
B(12A)-B(18A)-H(18B)	120.9
B(17A)-B(18A)-H(18B)	122.8
B(22A)-B(19A)-B(18A)	60.5(10)
B(22A)-B(19A)-B(14A)	109.4(12)
B(18A)-B(19A)-B(14A)	106.5(13)
B(22A)-B(19A)-B(13A)	108.0(13)
B(18A)-B(19A)-B(13A)	59.0(10)
B(14A)-B(19A)-B(13A)	58.6(10)

B(22A)-B(19A)-B(20A)	61.5(10)
B(18A)-B(19A)-B(20A)	109.1(13)
B(14A)-B(19A)-B(20A)	60.9(9)
B(13A)-B(19A)-B(20A)	108.0(12)
B(22A)-B(19A)-H(19C)	120.5
B(18A)-B(19A)-H(19C)	122.2
B(14A)-B(19A)-H(19C)	122.1
B(13A)-B(19A)-H(19C)	122.7
B(20A)-B(19A)-H(19C)	120.5
B(15A)-B(20A)-B(21A)	61.3(10)
B(15A)-B(20A)-B(22A)	107.5(13)
B(21A)-B(20A)-B(22A)	59.1(10)
B(15A)-B(20A)-B(19A)	108.2(13)
B(21A)-B(20A)-B(19A)	105.7(13)
B(22A)-B(20A)-B(19A)	57.0(9)
B(15A)-B(20A)-B(14A)	61.3(10)
B(21A)-B(20A)-B(14A)	108.4(13)
B(22A)-B(20A)-B(14A)	104.1(12)
B(19A)-B(20A)-B(14A)	58.8(10)
B(15A)-B(20A)-H(20O)	120.1
B(21A)-B(20A)-H(20O)	121.6
B(22A)-B(20A)-H(20O)	124.4
B(19A)-B(20A)-H(20O)	123.5
B(14A)-B(20A)-H(20O)	122.5
B(17A)-B(21A)-B(22A)	61.6(10)
B(17A)-B(21A)-B(16A)	59.2(10)
B(22A)-B(21A)-B(16A)	107.5(12)
B(17A)-B(21A)-B(20A)	109.1(12)
B(22A)-B(21A)-B(20A)	60.6(9)
B(16A)-B(21A)-B(20A)	105.6(12)
B(17A)-B(21A)-B(15A)	105.8(13)
B(22A)-B(21A)-B(15A)	106.2(12)
B(16A)-B(21A)-B(15A)	58.0(10)
B(20A)-B(21A)-B(15A)	58.1(9)
B(17A)-B(21A)-H(21H)	121.2
B(22A)-B(21A)-H(21H)	121.1
B(16A)-B(21A)-H(21H)	123.3
B(20A)-B(21A)-H(21H)	122.1
B(15A)-B(21A)-H(21H)	124.2
B(19A)-B(22A)-B(18A)	60.8(10)
B(19A)-B(22A)-B(21A)	110.3(13)
B(18A)-B(22A)-B(21A)	108.8(13)
B(19A)-B(22A)-B(17A)	108.6(13)
B(18A)-B(22A)-B(17A)	60.7(10)
B(21A)-B(22A)-B(17A)	58.2(10)
B(19A)-B(22A)-B(20A)	61.5(9)
B(18A)-B(22A)-B(20A)	109.4(13)
B(21A)-B(22A)-B(20A)	60.2(9)

B(17A)-B(22A)-B(20A)	106.1(12)
B(19A)-B(22A)-H(22K)	120.0
B(18A)-B(22A)-H(22K)	120.6
B(21A)-B(22A)-H(22K)	121.4
B(17A)-B(22A)-H(22K)	123.1
B(20A)-B(22A)-H(22K)	121.7
Cl(1S)-C(1S)-Cl(2S)	115.6(13)
Cl(1S)-C(1S)-H(1S1)	108.4
Cl(2S)-C(1S)-H(1S1)	108.4
Cl(1S)-C(1S)-H(1S2)	108.4
Cl(2S)-C(1S)-H(1S2)	108.4
H(1S1)-C(1S)-H(1S2)	107.4
C(2T)-C(1T)-H(1T1)	109.5
C(2T)-C(1T)-H(1T2)	109.5
H(1T1)-C(1T)-H(1T2)	109.5
C(2T)-C(1T)-H(1T3)	109.5
H(1T1)-C(1T)-H(1T3)	109.5
H(1T2)-C(1T)-H(1T3)	109.5
C(1T)-C(2T)-C(3T)	106(2)
C(1T)-C(2T)-H(2T1)	110.6
C(3T)-C(2T)-H(2T1)	110.6
C(1T)-C(2T)-H(2T2)	110.6
C(3T)-C(2T)-H(2T2)	110.6
H(2T1)-C(2T)-H(2T2)	108.8
C(4T)-C(3T)-C(2T)	97(2)
C(4T)-C(3T)-H(3T1)	112.3
C(2T)-C(3T)-H(3T1)	112.3
C(4T)-C(3T)-H(3T2)	112.3
C(2T)-C(3T)-H(3T2)	112.3
H(3T1)-C(3T)-H(3T2)	109.9
C(5T)-C(4T)-C(3T)	111(2)
C(5T)-C(4T)-H(4T1)	109.3
C(3T)-C(4T)-H(4T1)	109.3
C(5T)-C(4T)-H(4T2)	109.3
C(3T)-C(4T)-H(4T2)	109.3
H(4T1)-C(4T)-H(4T2)	108.0
C(4T)-C(5T)-H(5T1)	109.5
C(4T)-C(5T)-H(5T2)	109.5
H(5T1)-C(5T)-H(5T2)	109.5
C(4T)-C(5T)-H(5T3)	109.5
H(5T1)-C(5T)-H(5T3)	109.5
H(5T2)-C(5T)-H(5T3)	109.5
C(2U)-C(1U)-H(1U1)	109.5
C(2U)-C(1U)-H(1U2)	109.5
H(1U1)-C(1U)-H(1U2)	109.5
C(2U)-C(1U)-H(1U3)	109.5
H(1U1)-C(1U)-H(1U3)	109.5
H(1U2)-C(1U)-H(1U3)	109.5

C(1U)-C(2U)-C(3U)	117.9(18)
C(1U)-C(2U)-H(2U1)	107.8
C(3U)-C(2U)-H(2U1)	107.8
C(1U)-C(2U)-H(2U2)	107.8
C(3U)-C(2U)-H(2U2)	107.8
H(2U1)-C(2U)-H(2U2)	107.2
C(2U)-C(3U)-C(4U)	112.0(17)
C(2U)-C(3U)-H(3U1)	109.2
C(4U)-C(3U)-H(3U1)	109.2
C(2U)-C(3U)-H(3U2)	109.2
C(4U)-C(3U)-H(3U2)	109.2
H(3U1)-C(3U)-H(3U2)	107.9
C(3U)-C(4U)-C(5U)	109.4(16)
C(3U)-C(4U)-H(4U1)	109.8
C(5U)-C(4U)-H(4U1)	109.8
C(3U)-C(4U)-H(4U2)	109.8
C(5U)-C(4U)-H(4U2)	109.8
H(4U1)-C(4U)-H(4U2)	108.2
C(4U)-C(5U)-H(5U1)	109.5
C(4U)-C(5U)-H(5U2)	109.5
H(5U1)-C(5U)-H(5U2)	109.5
C(4U)-C(5U)-H(5U3)	109.5
H(5U1)-C(5U)-H(5U3)	109.5
H(5U2)-C(5U)-H(5U3)	109.5
C(2V)-C(1V)-H(1V1)	109.5
C(2V)-C(1V)-H(1V2)	109.5
H(1V1)-C(1V)-H(1V2)	109.5
C(2V)-C(1V)-H(1V3)	109.5
H(1V1)-C(1V)-H(1V3)	109.5
H(1V2)-C(1V)-H(1V3)	109.5
C(1V)-C(2V)-C(3V)	103(2)
C(1V)-C(2V)-H(2V1)	111.1
C(3V)-C(2V)-H(2V1)	111.1
C(1V)-C(2V)-H(2V2)	111.1
C(3V)-C(2V)-H(2V2)	111.1
H(2V1)-C(2V)-H(2V2)	109.1
C(4V)-C(3V)-C(2V)	108(2)
C(4V)-C(3V)-H(3V1)	110.1
C(2V)-C(3V)-H(3V1)	110.1
C(4V)-C(3V)-H(3V2)	110.1
C(2V)-C(3V)-H(3V2)	110.1
H(3V1)-C(3V)-H(3V2)	108.4
C(5V)-C(4V)-C(3V)	102(2)
C(5V)-C(4V)-H(4V1)	111.4
C(3V)-C(4V)-H(4V1)	111.4
C(5V)-C(4V)-H(4V2)	111.4
C(3V)-C(4V)-H(4V2)	111.4
H(4V1)-C(4V)-H(4V2)	109.2

C(4V)-C(5V)-H(5V1)	109.5
C(4V)-C(5V)-H(5V2)	109.5
H(5V1)-C(5V)-H(5V2)	109.5
C(4V)-C(5V)-H(5V3)	109.5
H(5V1)-C(5V)-H(5V3)	109.5
H(5V2)-C(5V)-H(5V3)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å ^{2}x 10^3) for syl004. The anisotropic displacement factor exponent takes the form: -2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U11	U22	U33	U23	U13	U12
Fe(1)	26(1)	35(1)	45(1)	-3(1)	-5(1)	-2(1)
C(1)	36(3)	35(3)	70(5)	2(5)	-9(4)	0(4)
C(2)	43(4)	30(5)	66(4)	5(3)	-18(3)	-4(4)
C(3)	45(4)	22(5)	57(3)	10(3)	-5(3)	-5(4)
C(4)	34(3)	26(5)	63(4)	10(4)	-7(3)	-4(3)
C(5)	38(4)	34(4)	65(4)	-3(4)	-13(3)	-4(3)
C(6)	46(5)	45(6)	101(9)	6(7)	0(6)	13(5)
C(7)	65(7)	37(9)	79(8)	26(7)	-37(6)	-16(7)
C(8)	80(10)	44(10)	47(5)	25(5)	17(6)	-7(7)
C(9)	30(2)	55(10)	75(11)	24(11)	1(4)	-8(4)
C(10)	72(10)	58(11)	75(8)	-17(8)	-21(6)	-8(9)
C(1A)	39(4)	33(4)	71(5)	0(5)	-7(4)	2(5)
C(2A)	36(3)	34(5)	72(5)	4(4)	-16(3)	-3(4)
C(3A)	42(4)	26(6)	59(3)	8(3)	-13(3)	-2(5)
C(4A)	33(3)	28(5)	60(4)	7(5)	-9(3)	-5(3)
C(5A)	37(4)	34(5)	61(4)	-1(5)	-11(3)	-6(4)
C(6A)	52(7)	40(8)	98(8)	-13(8)	4(7)	7(7)
C(7A)	40(5)	43(10)	99(10)	19(8)	-27(6)	-6(6)
C(8A)	59(9)	40(10)	52(3)	16(5)	-6(5)	-15(8)
C(9A)	31(3)	57(11)	65(12)	17(11)	-2(5)	-8(5)
C(10A)	65(9)	48(12)	68(6)	-8(8)	-22(6)	-18(8)
C(11)	24(3)	31(4)	27(3)	3(3)	1(2)	-3(3)
C(12)	21(3)	39(4)	33(3)	-5(3)	6(2)	-4(3)
C(13)	29(3)	66(6)	38(4)	-10(4)	7(3)	-4(4)
C(14)	43(4)	61(5)	22(3)	-5(3)	5(3)	-9(4)
C(15)	26(3)	28(4)	25(3)	6(3)	0(2)	-4(3)
C(16)	30(3)	36(4)	25(3)	13(3)	-3(3)	-7(3)
N(2)	26(3)	50(4)	38(3)	15(3)	-2(2)	-6(3)
C(19)	41(4)	96(7)	20(3)	10(4)	-10(3)	-15(4)
C(20)	37(4)	104(8)	39(4)	6(5)	-3(3)	-12(5)
C(21)	39(4)	62(6)	54(4)	28(4)	-21(4)	-11(4)
C(22)	24(3)	69(6)	50(4)	22(4)	-6(3)	-6(4)
C(17)	24(3)	40(5)	43(4)	9(3)	0(3)	9(3)
C(18)	36(3)	37(4)	30(3)	-4(3)	2(3)	4(3)
N(1)	21(2)	33(3)	27(2)	-1(2)	0(2)	2(2)
C(23)	31(3)	43(5)	31(3)	-7(3)	-3(3)	3(3)
O(1)	37(2)	65(4)	46(3)	-20(3)	-20(2)	18(3)
C(24)	42(4)	47(5)	35(4)	-3(3)	-9(3)	8(4)
F(1)	48(2)	45(3)	38(2)	-7(2)	-3(2)	12(2)
C(25)	50(4)	62(6)	31(4)	-18(4)	-2(3)	-2(4)
C(26)	42(4)	71(7)	32(4)	-23(4)	-4(3)	-11(4)
C(27)	66(5)	61(6)	40(4)	-22(4)	7(4)	-19(5)
C(28)	84(6)	78(7)	55(5)	-17(5)	3(5)	-36(6)

C(29)	59(5)	114(10)	44(5)	-17(5)	3(4)	-50(6)
C(30)	49(5)	90(8)	49(5)	-21(5)	4(4)	-24(5)
C(31)	38(4)	75(6)	41(4)	-17(4)	-7(3)	-2(4)
C(32)	43(4)	50(5)	26(3)	-9(3)	-8(3)	2(4)
C(33)	56(5)	77(7)	41(4)	8(4)	-1(4)	22(5)
C(34)	77(6)	69(7)	51(5)	13(5)	-8(4)	19(5)
C(35)	68(5)	63(6)	38(4)	0(4)	-2(4)	-17(5)
C(36)	56(5)	65(6)	59(5)	-8(5)	24(4)	-5(5)
C(37)	56(4)	41(5)	53(4)	-13(4)	9(4)	-3(4)
Fe(2)	22(1)	45(2)	24(1)	8(1)	1(1)	-3(1)
C(201)	28(2)	53(4)	32(4)	12(3)	-2(3)	1(2)
C(202)	34(3)	63(5)	24(3)	13(3)	-3(2)	-7(3)
C(203)	34(3)	63(4)	27(3)	13(3)	2(2)	-8(3)
C(204)	36(3)	52(3)	34(4)	13(3)	-3(3)	-9(3)
C(205)	37(3)	46(3)	30(4)	10(3)	-1(3)	0(2)
C(206)	28(3)	53(10)	52(9)	12(7)	1(4)	6(4)
C(207)	43(6)	72(10)	25(4)	12(4)	-6(4)	-8(6)
C(208)	43(5)	75(11)	41(5)	26(6)	15(4)	7(7)
C(209)	45(5)	53(8)	59(8)	9(6)	-9(6)	-15(6)
C(210)	58(7)	48(6)	35(7)	7(5)	-1(5)	12(5)
C(211)	33(2)	45(3)	22(2)	4(2)	0(2)	3(2)
C(212)	28(2)	65(4)	33(2)	11(2)	1(2)	7(2)
C(213)	42(2)	66(4)	34(3)	4(2)	12(2)	15(2)
C(214)	51(3)	50(2)	26(2)	-4(2)	7(2)	6(2)
C(215)	37(2)	40(3)	20(2)	1(2)	3(2)	0(2)
C(216)	37(2)	24(3)	24(2)	0(2)	2(2)	-1(2)
N(202)	41(2)	35(3)	32(2)	-5(2)	-2(2)	-3(2)
C(219)	60(3)	53(5)	34(3)	-10(3)	-9(2)	-7(3)
C(220)	68(4)	69(5)	55(3)	-11(4)	-21(3)	-17(4)
C(221)	51(3)	46(5)	64(4)	2(3)	-19(3)	-11(3)
C(222)	41(3)	41(4)	47(3)	3(3)	-3(2)	-9(3)
C(217)	36(3)	31(4)	24(2)	0(2)	4(2)	1(2)
C(218)	44(3)	34(4)	21(2)	-4(2)	4(2)	-1(3)
N(201)	42(2)	37(3)	21(2)	2(2)	0(2)	-7(2)
C(223)	54(4)	38(6)	31(3)	2(4)	-2(3)	-16(5)
O(201)	54(7)	60(11)	43(5)	5(8)	-2(5)	-23(7)
C(224)	66(4)	35(3)	32(4)	-2(3)	-10(3)	-8(3)
F(201)	47(6)	35(5)	26(7)	-2(6)	-2(6)	10(5)
C(225)	67(5)	47(6)	37(5)	-5(4)	-11(4)	-9(4)
C(226)	55(4)	52(6)	43(5)	-2(4)	-9(4)	-10(4)
C(227)	54(6)	56(8)	47(6)	7(5)	-7(4)	-3(5)
C(228)	55(6)	58(8)	45(7)	5(5)	-11(5)	0(5)
C(229)	52(6)	61(7)	49(8)	9(5)	-7(5)	5(6)
C(230)	51(6)	64(6)	52(7)	8(5)	-5(5)	4(5)
C(231)	47(6)	61(6)	47(7)	7(5)	-8(5)	1(5)
C(232)	83(5)	37(3)	38(5)	0(4)	-12(4)	-2(4)
C(233)	93(7)	34(4)	42(6)	-1(5)	-14(5)	-5(5)
C(234)	94(7)	38(4)	52(7)	6(5)	-24(5)	0(6)

C(235)	101(8)	38(5)	66(7)	0(5)	-15(6)	5(5)
C(236)	99(7)	40(5)	60(6)	5(5)	-11(5)	12(4)
C(237)	87(7)	41(4)	43(5)	5(5)	-11(5)	10(4)
Fe(2B)	30(4)	62(5)	21(2)	3(3)	3(2)	-5(3)
C(01B)	34(4)	54(7)	23(5)	15(5)	0(4)	-6(4)
C(02B)	38(5)	58(7)	25(4)	8(5)	0(4)	-7(5)
C(03B)	36(5)	62(6)	28(4)	8(4)	5(4)	-5(5)
C(04B)	32(5)	61(5)	27(5)	11(5)	-1(4)	-5(5)
C(05B)	31(5)	55(5)	22(5)	12(5)	-2(4)	-2(5)
C(06B)	32(4)	48(15)	38(11)	4(12)	1(6)	-3(6)
C(07B)	56(12)	67(16)	31(6)	2(8)	-13(6)	2(10)
C(08B)	54(10)	71(16)	42(7)	10(9)	21(8)	-6(12)
C(09B)	31(8)	60(10)	43(11)	4(10)	1(8)	-3(9)
C(10B)	55(11)	53(11)	29(8)	5(8)	6(7)	-2(10)
C(23B)	54(6)	38(7)	30(4)	6(4)	-2(3)	-10(5)
O(01B)	50(8)	45(9)	36(4)	26(7)	-11(5)	-9(6)
C(24B)	68(4)	34(4)	29(4)	1(4)	-8(4)	-7(3)
F(01B)	56(7)	44(5)	30(7)	13(7)	-2(7)	2(6)
C(25B)	67(4)	45(5)	33(5)	-6(5)	-8(4)	-10(4)
C(26B)	53(4)	52(6)	42(5)	-1(4)	-7(4)	-7(4)
C(27B)	51(5)	61(7)	48(6)	1(5)	-6(4)	-4(5)
C(28B)	53(5)	67(8)	53(7)	1(6)	-5(5)	2(5)
C(29B)	49(6)	66(7)	54(8)	4(5)	-12(5)	5(5)
C(30B)	52(7)	65(6)	53(7)	11(5)	-9(5)	7(6)
C(31B)	46(6)	61(6)	47(7)	10(4)	-10(4)	2(5)
C(32B)	82(5)	37(3)	33(5)	-3(4)	-14(4)	1(4)
C(33B)	89(6)	37(4)	52(6)	1(5)	-13(5)	3(4)
C(34B)	100(7)	38(4)	61(7)	-4(5)	-16(6)	7(5)
C(35B)	101(7)	40(5)	68(7)	7(6)	-13(6)	19(6)
C(36B)	91(7)	40(6)	57(6)	1(6)	-15(6)	17(5)
C(37B)	80(6)	36(5)	34(5)	-3(5)	-15(5)	9(4)
C(101)	56(4)	65(6)	38(4)	11(4)	8(3)	10(5)
B(1)	31(4)	42(5)	48(5)	4(4)	5(3)	1(4)
B(2)	32(4)	57(6)	48(4)	14(4)	12(3)	11(4)
B(3)	45(4)	45(5)	35(4)	4(4)	13(3)	7(4)
B(4)	30(4)	62(6)	43(4)	5(5)	-1(3)	-5(4)
B(5)	26(3)	39(5)	38(4)	9(4)	4(3)	6(3)
B(6)	35(4)	48(5)	33(4)	6(3)	-1(3)	5(4)
B(7)	30(4)	45(6)	57(5)	-2(4)	1(3)	5(4)
B(8)	33(4)	43(5)	43(4)	9(4)	1(3)	2(4)
B(9)	40(4)	42(5)	40(4)	10(4)	5(3)	2(4)
B(10)	36(4)	54(6)	38(4)	14(4)	9(3)	5(4)
B(11)	43(4)	55(6)	26(4)	7(4)	2(3)	11(4)
C(102)	62(4)	83(4)	75(4)	-13(3)	-6(3)	20(3)
B(12)	58(4)	77(4)	66(4)	8(3)	-11(3)	8(3)
B(13)	53(3)	88(4)	67(4)	7(4)	-12(3)	14(3)
B(14)	47(3)	107(5)	64(4)	3(4)	-6(3)	12(3)
B(15)	48(4)	97(5)	51(3)	-12(3)	-2(2)	13(4)

B(16)	53(3)	74(5)	60(4)	-4(4)	-11(3)	4(4)
B(17)	51(3)	84(5)	49(3)	6(4)	1(3)	15(3)
B(18)	66(4)	83(5)	47(3)	3(3)	-10(3)	12(4)
B(19)	63(4)	89(5)	57(4)	4(3)	-19(3)	-2(3)
B(20)	54(4)	91(4)	55(4)	9(3)	-10(3)	-3(3)
B(21)	48(3)	74(4)	39(3)	-4(3)	-4(3)	8(3)
B(22)	75(4)	75(4)	45(4)	-5(3)	-16(3)	11(3)
C(02A)	54(5)	89(4)	66(4)	-8(4)	-7(4)	9(4)
B(12A)	57(5)	84(5)	68(4)	1(4)	-6(4)	8(4)
B(13A)	54(4)	88(5)	64(5)	-5(4)	-7(4)	10(4)
B(14A)	56(4)	94(5)	58(4)	-5(4)	-3(4)	9(4)
B(15A)	55(4)	92(5)	56(3)	-4(4)	-8(3)	9(4)
B(16A)	53(4)	86(5)	62(5)	-3(4)	-6(3)	7(4)
B(17A)	56(5)	87(6)	57(3)	1(4)	-6(4)	10(4)
B(18A)	56(4)	87(6)	60(4)	-1(4)	-8(4)	10(4)
B(19A)	52(4)	89(5)	62(5)	-1(4)	-7(3)	7(4)
B(20A)	54(4)	89(4)	58(4)	1(4)	-5(4)	7(4)
B(21A)	53(4)	85(5)	54(4)	-1(4)	-6(4)	9(4)
B(22A)	56(5)	85(5)	58(4)	-2(4)	-9(4)	8(4)
C(1S)	121(9)	98(9)	133(7)	-39(7)	-32(7)	-30(7)
Cl(1S)	89(3)	137(4)	101(3)	-17(3)	30(2)	2(3)
Cl(2S)	166(6)	162(6)	169(6)	29(4)	-63(4)	-74(5)
C(1T)	132(7)	119(7)	146(7)	-16(7)	-23(7)	-42(7)
C(2T)	132(7)	119(7)	146(7)	-16(7)	-23(7)	-42(7)
C(3T)	132(7)	119(7)	146(7)	-16(7)	-23(7)	-42(7)
C(4T)	132(7)	119(7)	146(7)	-16(7)	-23(7)	-42(7)
C(5T)	132(7)	119(7)	146(7)	-16(7)	-23(7)	-42(7)
C(1U)	204(13)	75(11)	161(14)	-3(10)	89(12)	-30(12)
C(2U)	196(10)	111(10)	203(11)	-39(9)	93(10)	-33(11)
C(3U)	196(10)	109(10)	214(10)	-36(9)	88(10)	-30(11)
C(4U)	170(11)	96(10)	209(11)	-53(8)	72(10)	-52(10)
C(5U)	101(11)	94(12)	190(10)	-94(9)	12(10)	-48(10)
C(1V)	168(17)	75(15)	208(12)	-26(10)	81(15)	-15(16)
C(2V)	184(12)	107(10)	211(11)	-39(9)	83(11)	-33(11)
C(3V)	187(12)	112(10)	202(11)	-39(9)	84(11)	-33(12)
C(4V)	165(13)	102(12)	202(11)	-46(10)	61(12)	-49(13)
C(5V)	153(18)	104(12)	209(19)	-44(12)	41(18)	-44(17)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^{2}x 10 ^{3}) for syl004.

	x	y	z	U(eq)
H(6A)	5586	6442	3528	96
H(6B)	6218	7192	3660	96
H(6C)	6029	6413	3920	96
H(7A)	5689	5921	2990	91
H(7B)	6227	5197	2785	91
H(7C)	6436	6158	2698	91
H(8A)	7763	4770	2675	86
H(8B)	8717	4655	2868	86
H(8C)	8500	5498	2653	86
H(9A)	9498	4905	3398	80
H(9B)	9454	5352	3781	80
H(9C)	9698	5886	3431	80
H(10A)	7551	6236	4238	103
H(10B)	8056	7009	4053	103
H(10C)	8595	6165	4138	103
H(6A1)	6360	7096	3966	95
H(6A2)	6379	6255	4199	95
H(6A3)	5674	6353	3877	95
H(7A1)	5713	5465	3080	91
H(7A2)	6000	6360	2924	91
H(7A3)	5491	6298	3301	91
H(8A1)	8111	4798	2819	76
H(8A2)	8145	5741	2675	76
H(8A3)	7207	5251	2690	76
H(9A1)	9632	5874	3338	76
H(9A2)	9309	4953	3227	76
H(9A3)	9505	5170	3639	76
H(10D)	8891	5778	4153	91
H(10E)	7926	5922	4333	91
H(10F)	8460	6696	4163	91
H(12)	5640	4184	3400	37
H(13)	5834	4641	4041	53
H(14)	7386	4268	4250	50
H(19A)	8634	3537	4443	63
H(19B)	8740	4430	4248	63
H(20A)	10241	4484	4353	72
H(20B)	9966	3910	4691	72
H(21A)	10338	2710	4406	62
H(21B)	11091	3331	4248	62
H(22A)	10385	3432	3701	57
H(22B)	10032	2510	3810	57
H(17)	9251	2811	3295	43

H(18)	8208	2718	2861	41
H(25A)	5364	2837	2324	57
H(25B)	5811	1995	2176	57
H(27)	5838	738	2561	67
H(28)	5108	-54	2997	87
H(29)	4015	601	3362	87
H(30)	3708	2000	3303	75
H(31)	4454	2803	2872	62
H(33)	6576	4163	2224	70
H(34)	7426	4792	1789	79
H(35)	8642	4058	1527	68
H(36)	8907	2682	1700	72
H(37)	8023	2051	2134	60
H(20C)	553	5338	5417	66
H(20D)	852	4865	5776	66
H(20E)	775	4358	5407	66
H(20F)	1914	4715	4606	70
H(20G)	1484	4052	4879	70
H(20H)	2493	3929	4739	70
H(20I)	3911	5532	4688	80
H(20J)	3915	4539	4746	80
H(20K)	4578	5120	4975	80
H(20L)	4703	5801	5495	78
H(20M)	4218	5993	5869	78
H(20N)	4133	6643	5544	78
H(21C)	2788	5932	6175	71
H(21D)	1763	5650	6124	71
H(21E)	2091	6541	5977	71
H(212)	4623	4201	5889	51
H(213)	4322	3429	5311	57
H(214)	2764	2831	5318	51
H(21F)	1516	2022	5448	59
H(21G)	1343	2950	5293	59
H(22C)	141	1801	5223	77
H(22D)	-145	2767	5266	77
H(22E)	-129	1514	5809	65
H(22F)	-903	2198	5733	65
H(22G)	-131	3233	6014	51
H(22H)	272	2454	6236	51
H(217)	1076	3500	6465	36
H(218)	2165	4180	6763	40
H(22I)	4346	5047	7425	60
H(22J)	4880	5428	7086	60
H(227)	5783	4362	6685	63
H(228)	6537	3092	6675	64
H(229)	6350	2107	7114	65
H(230)	5283	2340	7574	67
H(231)	4482	3596	7588	62

H(233)	4356	6222	6662	68
H(234)	3705	7578	6670	73
H(235)	2355	7762	7004	82
H(236)	1647	6705	7242	80
H(237)	2349	5372	7278	68
H(06A)	785	4876	5846	59
H(06B)	594	4632	5437	59
H(06C)	496	5584	5565	59
H(07A)	1440	5100	4725	77
H(07B)	1426	4218	4928	77
H(07C)	2275	4474	4689	77
H(08A)	3742	5001	4728	83
H(08B)	4442	5391	5008	83
H(08C)	3797	5994	4781	83
H(09A)	4550	6118	5540	67
H(09B)	4106	6161	5931	67
H(09C)	3883	6869	5640	67
H(10G)	1725	6395	6101	69
H(10H)	2737	6198	6221	69
H(10I)	1981	5489	6253	69
H(25C)	5080	5117	6967	58
H(25D)	4729	5077	7371	58
H(27B)	5943	4014	6747	64
H(28B)	6635	2730	6818	69
H(29B)	6147	1830	7272	67
H(30B)	5031	2229	7667	68
H(31B)	4421	3571	7625	61
H(33B)	3919	6422	6812	71
H(34B)	3100	7635	6825	80
H(35B)	1625	7547	7109	84
H(36B)	1092	6278	7315	75
H(37B)	1963	5061	7266	60
H(101)	3077	4226	4124	64
H(1)	2090	3228	3624	48
H(2)	1315	4770	3947	55
H(3)	2753	5958	4048	50
H(4)	4452	5197	3799	54
H(5)	4038	3521	3538	41
H(6)	2819	3683	2927	46
H(7)	1123	4450	3174	52
H(8)	1539	6127	3432	48
H(9)	3492	6425	3348	49
H(10)	4263	4890	3022	51
H(11)	2484	5471	2805	50
H(102)	2840	9209	4198	88
H(12A)	1615	9241	4801	81
H(13A)	3572	9680	4858	83
H(14A)	4109	10464	4193	87

H(15)	2491	10499	3704	78
H(16)	1015	9744	4096	75
H(17A)	644	10796	4716	74
H(18A)	2246	10758	5190	79
H(19)	3703	11526	4813	84
H(20)	3096	11977	4056	80
H(21)	1154	11580	4050	65
H(22)	1964	12200	4719	78
H(02A)	2020	9031	4141	84
H(12B)	2093	8845	4913	84
H(13B)	3749	9167	4490	83
H(14B)	3295	10254	3909	84
H(15A)	1343	10721	3962	81
H(16A)	633	9816	4561	81
H(17B)	1505	10411	5210	80
H(18B)	3464	10036	5159	81
H(19C)	4163	10971	4548	81
H(20O)	2666	11897	4202	80
H(21H)	1087	11608	4668	77
H(22K)	2860	11711	4999	79
H(1S1)	8737	7354	6379	141
H(1S2)	8522	6458	6210	141
H(1T1)	9405	6618	6604	199
H(1T2)	10259	6625	6343	199
H(1T3)	9386	6092	6239	199
H(2T1)	9421	7880	6274	159
H(2T2)	8554	7336	6161	159
H(3T1)	10070	7716	5692	159
H(3T2)	9847	6723	5688	159
H(4T1)	8278	7007	5597	159
H(4T2)	8444	7992	5642	159
H(5T1)	8257	7627	5031	199
H(5T2)	9125	7037	5056	199
H(5T3)	9228	8030	5098	199
H(1U1)	8232	7557	4991	220
H(1U2)	7463	7745	4702	220
H(1U3)	7444	6892	4928	220
H(2U1)	7211	8506	5222	204
H(2U2)	7219	7666	5452	204
H(3U1)	5839	7257	5194	208
H(3U2)	5833	8088	4954	208
H(4U1)	4891	8360	5446	190
H(4U2)	5780	8910	5509	190
H(5U1)	5393	8152	6054	193
H(5U2)	6361	7860	5914	193
H(5U3)	5497	7285	5843	193
H(1V1)	6668	8107	4602	226
H(1V2)	5971	7357	4662	226

H(1V3)	6997	7253	4784	226
H(2V1)	5720	8379	5129	201
H(2V2)	6764	8328	5243	201
H(3V1)	5486	6936	5287	200
H(3V2)	6546	6791	5343	200
H(4V1)	5418	7221	5886	188
H(4V2)	6497	7310	5914	188
H(5V1)	5870	8680	5983	233
H(5V2)	5310	8572	5619	233
H(5V3)	6382	8653	5605	233

VI. Mechanistic/Reactivity Studies

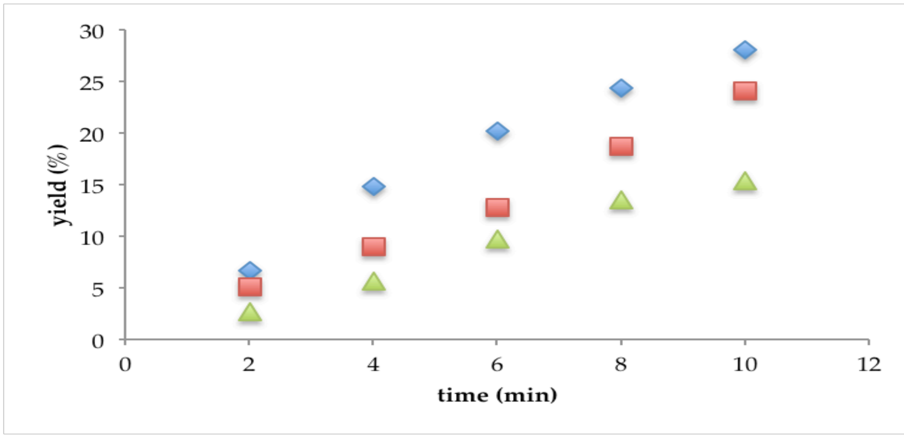


Figure 1. Comparison of reaction rates: fluorination of phenyl methyl ketene (blue), phenyl ethyl ketene (red), and phenyl isobutyl ketene (green) catalyzed by PPY*. In a nitrogen-filled glovebox, NFSI (15.8 mg, 0.050 mmol), tetradecane (13 µL, 0.050 mmol; internal standard), and THF (37.8 mL) were combined in an oven-dried 50-mL round-bottom flask equipped with a stir bar. The flask was fitted with a rubber septum, and then the flask was removed from the glovebox. A nitrogen-filled balloon was attached to the flask, which was cooled to –78 °C. Next a solution of **PPY*** (0.188 mg in 0.050 mL of THF; 0.50 µmol) was added to the flask via syringe. Then, a solution of the ketene (0.050 mmol in 0.10 mL of THF) and a solution of C_6F_5ONa (10.3 mg in 0.10 mL of THF; 0.050 mmol) were added dropwise to the flask simultaneously over 8 seconds. An aliquot (1.00 mL) of the reaction mixture was removed after 2 min, 4 min, 6 min, 8 min, and 10 min and quenched with 1.0 mL of methanol (a syringe with a long metal needle that contained 1.0 mL of MeOH was used to take an aliquot of the reaction mixture). The amount of product was determined by GC analysis.

yield / time (min)	phenyl methyl ketene	phenyl ethyl ketene	phenyl isobutyl ketene
0	0	0	0
2	6.7	5.1	2.7
4	15	9.0	5.7
6	20	13	9.7
8	24	19	14
10	28	24	15

Determination of the rate law: fluorination of phenyl ethyl ketene. In a nitrogen-filled glovebox, NFSI, hexadecane (internal standard), and THF (37.8 mL) were combined in an oven-dried 50-mL round-bottom flask equipped with a stir bar. The flask was fitted with a rubber septum, and then the flask was removed from the glovebox. A nitrogen-filled balloon was attached to the flask, which was cooled to –78 °C. Next a solution of **PPY*** (in 0.050 mL of THF) was added to the flask via syringe. Then, a solution of the ketene (in 0.10 mL of THF) and a solution of C_6F_5ONa (in 0.10 mL of THF) were added dropwise to the flask simultaneously over 8 seconds. An aliquot (1.00 mL) of the reaction mixture was removed after 2 min, 4 min, 6 min, 8 min, and 10 min, and quenched with 1.0 mL of methanol (a syringe with a long metal needle that contained 1.0 mL of MeOH was used to take an aliquot of the reaction mixture). The amount of product was determined by GC analysis.

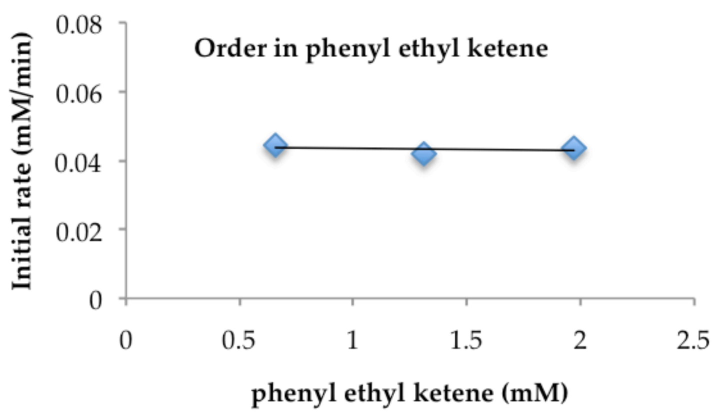
Order in phenyl ethyl ketene:

Table S1. Observed Initial Rates

[phenyl ethyl ketene]$_{initial}$ (mM)[a]	k_{obs} (mM/min)
0.657	0.044
1.31	0.042
1.97	0.044

[a] Reaction conditions: [NFSI]$_{initial}$ = 1.31 mM, [C_6F_5ONa]$_{initial}$ = 1.31 mM, and [**PPY***]$_{initial}$ = 0.0131 mM.

Figure S1.



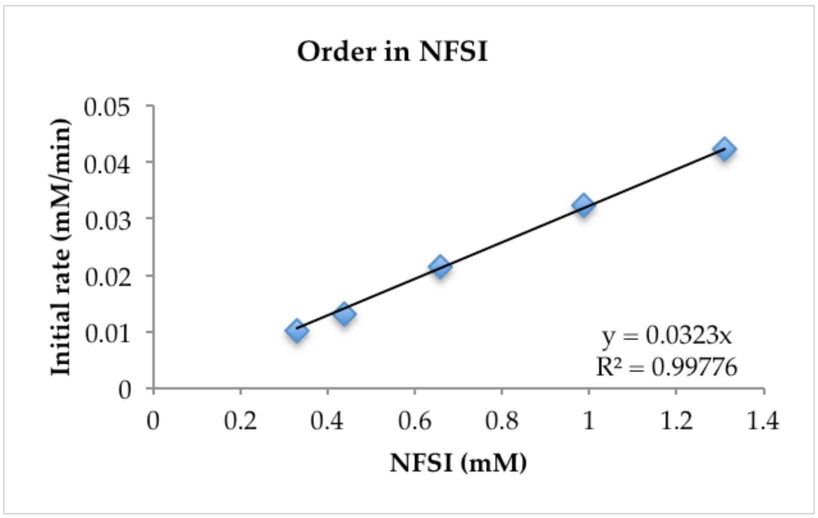
Order in NFSI:

Table S2. Observed Initial Rates

$[NFSI]_{initial}$ (mM)[a]	k_{obs} (mM/min)
0.329	0.010
0.437	0.013
0.657	0.022
0.986	0.032
1.31	0.042

[a] Reaction conditions: [phenyl ethyl ketene]$_{initial}$ = 1.31 mM, $[C_6F_5ONa]_{initial}$ = 1.31 mM, and **[PPY*]**$_{initial}$ = 0.0131 mM.

Figure S2.



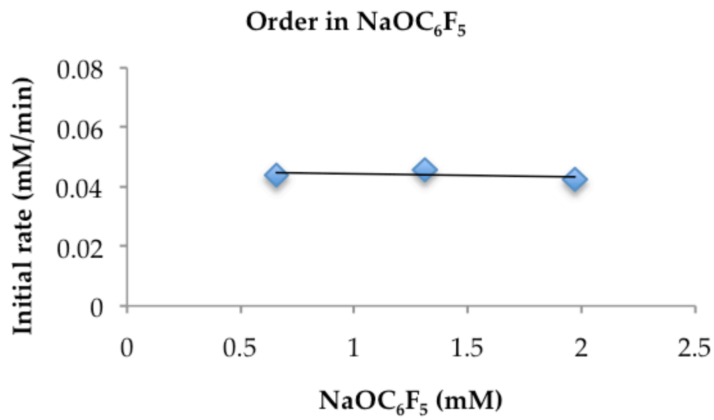
Order in C_6F_5ONa:

Table S3. Observed Initial Rates

$[C_6F_5ONa]_{initial}$ (mM)[a]	k_{obs} (mM/min)
0.657	0.044
0.986	0.046
1.31	0.042

[a] Reaction conditions: [phenyl ethyl ketene]$_{initial}$ = 1.31 mM, $[NFSI]_{initial}$= 1.31 mM, and $[PPY^*]_{initial}$ = 0.0131 mM.

Figure S3.



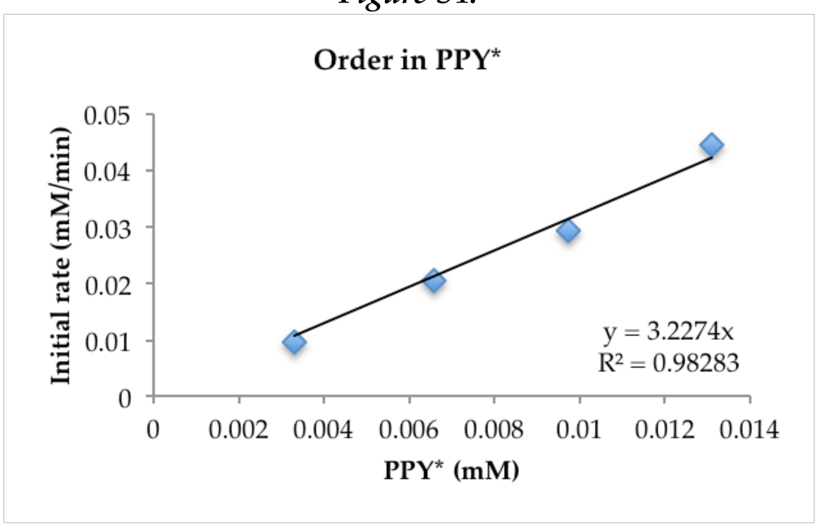
Order in PPY*:

Table S4. Observed Initial Rates

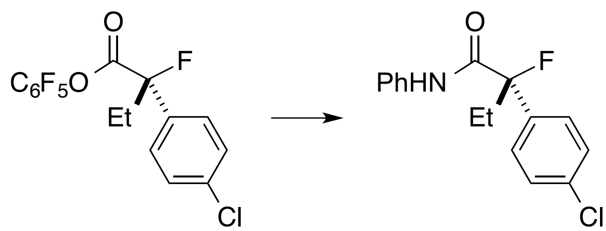
[PPY*]$_{initial}$ (mM)[a]	k_{obs} (mM/min)
0.00329	0.0096
0.00657	0.020
0.00972	0.029
0.0131	0.044

[a] Reaction conditions: [phenyl ethyl ketene]$_{initial}$ = 1.31 mM, [NFSI]$_{initial}$= 1.31 mM, and $[C_6F_5ONa]_{initial}$ = 1.31 mM.

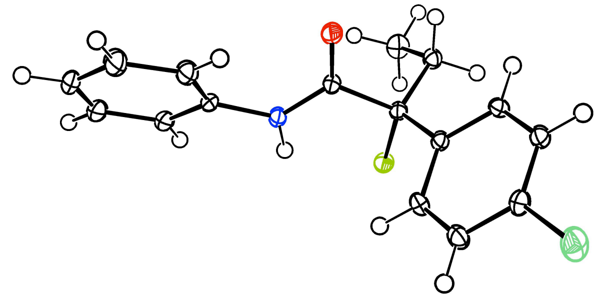
Figure S4.



VII. Determination of Absolute Configuration



(*R*)-2-(4-Chlorophenyl)-2-fluoro-*N*-phenylbutanamide (derived from the product of Table 2, entry 6). (*R*)-Perfluorophenyl 2-(4-chlorophenyl)-2-fluorobutanoate (38.3 mg, 0.10 mmol; 97% ee, obtained with (+)-**PPY***), aniline (14.0 mg, 0.15 mmol), Et_3N (20 μL), and THF (1.0 mL) were added to a 4-mL vial, which was then sealed and heated at 65 °C for 12 h. The mixture was then allowed to cool to r.t., and the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexanes → 10% Et_2O in hexanes), which furnished the product as a white solid (29 mg, 99% yield). X-ray quality crystals were obtained by cooling a saturated solution in ethanol. The absolute stereochemistry was determined to be (*R*) by X-ray crystallography. The absolute configurations of other fluorinated products (from aryl alkyl ketenes) were assigned by analogy.



A crystal of $C_{16}H_{15}ClFNO$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Apex II diffractometer with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using least squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter. Density corresponding to approximately 24 electrons per unit cell could not be modeled in a chemically reasonable manner and was removed using Platon/Squeeze, leaving voids totaling 166 cubic angstroms. The use of Squeeze does not change the interpretation of the chemical absolute stereochemistry.

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* (2009). 42, 339-341.
[2] SHELXS, G.M. Sheldrick, *Acta Cryst.* (2008). A64, 112–122.
[3] SHELXL, G.M. Sheldrick, *Acta Cryst.* (2008). A64, 112–122.

Table 1. Crystal data and structure refinement for 002.

Identification code	syl002-sr	
Empirical formula	$C_{16} H_{15} Cl F N O$	
Formula weight	291.74	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	$P6_1$	
Unit cell dimensions	a = 21.7099(11) Å	α = 90°.
	b = 21.7099(11) Å	β = 90 °.
	c = 5.3925(3) Å	γ = 120 °.
Volume	2201.1(3) $Å^3$	
Z	6	
Density (calculated)	1.321 Mg/m^3	
Absorption coefficient	0.266 mm^{-1}	
F(000)	912	
Crystal size	0.38 x 0.12 x 0.03 mm^3	
Theta range for data collection	1.876 to 35.120°.	
Index ranges	-34<=h<=34, -34<=k<=34, -8<=l<=8	
Reflections collected	51350	
Independent reflections	6146 [R(int) = 0.0653]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8720	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6146 / 1 / 241	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.0932	
R indices (all data)	R1 = 0.0591, wR2 = 0.0989	
Absolute structure parameter (Flack)	0.03(2)	
Largest diff. peak and hole	0.376 and -0.234 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 002. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	15063(1)	3609(1)	3361(1)	27(1)
F(1)	13136(1)	4755(1)	-2250(2)	17(1)
N(1)	11893(1)	3720(1)	-1195(3)	14(1)
O(1)	12102(1)	3852(1)	2988(2)	19(1)
C(1)	13056(1)	4635(1)	345(3)	13(1)
C(2)	12295(1)	4024(1)	835(3)	13(1)
C(3)	11181(1)	3144(1)	-1228(3)	14(1)
C(4)	10763(1)	3099(1)	-3257(3)	18(1)
C(5)	10072(1)	2536(1)	-3452(4)	25(1)
C(6)	9800(1)	2012(1)	-1649(4)	29(1)
C(7)	10220(1)	2058(1)	366(4)	29(1)
C(8)	10911(1)	2624(1)	598(3)	21(1)
C(9)	13577(1)	4397(1)	1111(3)	13(1)
C(10)	13988(1)	4652(1)	3252(3)	15(1)
C(11)	14448(1)	4413(1)	3933(3)	16(1)
C(12)	14499(1)	3921(1)	2459(3)	16(1)
C(13)	14099(1)	3659(1)	311(4)	18(1)
C(14)	13634(1)	3895(1)	-347(3)	16(1)
C(15)	13170(1)	5316(1)	1562(3)	16(1)
C(16)	12760(1)	5625(1)	274(4)	22(1)

Table 3. Bond lengths [Å] and angles [°] for 002.

Cl(1)-C(12)	1.7386(18)
F(1)-C(1)	1.4180(19)
N(1)-H(1)	0.83(3)
N(1)-C(2)	1.349(2)
N(1)-C(3)	1.421(2)
O(1)-C(2)	1.228(2)
C(1)-C(2)	1.537(2)
C(1)-C(9)	1.518(2)
C(1)-C(15)	1.521(2)
C(3)-C(4)	1.394(2)
C(3)-C(8)	1.387(2)
C(4)-H(4)	0.91(3)
C(4)-C(5)	1.387(3)
C(5)-H(5)	0.93(3)
C(5)-C(6)	1.385(3)
C(6)-H(6)	0.92(2)
C(6)-C(7)	1.390(3)
C(7)-H(7)	0.83(3)
C(7)-C(8)	1.390(3)
C(8)-H(8)	0.93(3)
C(9)-C(10)	1.393(2)
C(9)-C(14)	1.398(2)
C(10)-H(10)	0.93(3)
C(10)-C(11)	1.385(2)
C(11)-H(11)	0.97(3)
C(11)-C(12)	1.380(3)
C(12)-C(13)	1.388(2)
C(13)-H(13)	0.98(2)
C(13)-C(14)	1.387(3)
C(14)-H(14)	0.94(2)
C(15)-H(15A)	0.94(3)
C(15)-H(15B)	0.94(3)
C(15)-C(16)	1.523(3)
C(16)-H(16A)	1.01(3)
C(16)-H(16B)	1.00(3)
C(16)-H(16C)	1.00(3)
C(2)-N(1)-H(1)	119.0(18)
C(2)-N(1)-C(3)	126.41(15)
C(3)-N(1)-H(1)	114.5(17)
F(1)-C(1)-C(2)	107.97(13)
F(1)-C(1)-C(9)	106.65(13)
F(1)-C(1)-C(15)	107.61(13)
C(9)-C(1)-C(2)	108.76(13)
C(9)-C(1)-C(15)	115.27(14)
C(15)-C(1)-C(2)	110.29(14)

N(1)-C(2)-C(1)	115.81(14)
O(1)-C(2)-N(1)	125.45(16)
O(1)-C(2)-C(1)	118.74(15)
C(4)-C(3)-N(1)	117.07(15)
C(8)-C(3)-N(1)	122.58(15)
C(8)-C(3)-C(4)	120.29(16)
C(3)-C(4)-H(4)	117.9(17)
C(5)-C(4)-C(3)	120.10(18)
C(5)-C(4)-H(4)	121.8(17)
C(4)-C(5)-H(5)	123.2(19)
C(6)-C(5)-C(4)	120.00(19)
C(6)-C(5)-H(5)	116.6(19)
C(5)-C(6)-H(6)	121.6(17)
C(5)-C(6)-C(7)	119.62(18)
C(7)-C(6)-H(6)	118.8(17)
C(6)-C(7)-H(7)	119(2)
C(6)-C(7)-C(8)	120.9(2)
C(8)-C(7)-H(7)	120(2)
C(3)-C(8)-C(7)	119.04(18)
C(3)-C(8)-H(8)	121.0(16)
C(7)-C(8)-H(8)	119.9(16)
C(10)-C(9)-C(1)	121.91(15)
C(10)-C(9)-C(14)	119.14(15)
C(14)-C(9)-C(1)	118.93(14)
C(9)-C(10)-H(10)	122.7(16)
C(11)-C(10)-C(9)	120.61(16)
C(11)-C(10)-H(10)	116.6(16)
C(10)-C(11)-H(11)	121.0(15)
C(12)-C(11)-C(10)	119.28(16)
C(12)-C(11)-H(11)	119.7(15)
C(11)-C(12)-Cl(1)	119.05(14)
C(11)-C(12)-C(13)	121.46(16)
C(13)-C(12)-Cl(1)	119.48(14)
C(12)-C(13)-H(13)	121.0(14)
C(14)-C(13)-C(12)	118.94(16)
C(14)-C(13)-H(13)	120.1(14)
C(9)-C(14)-H(14)	120.1(14)
C(13)-C(14)-C(9)	120.56(15)
C(13)-C(14)-H(14)	119.4(14)
C(1)-C(15)-H(15A)	107.1(16)
C(1)-C(15)-H(15B)	108.6(15)
C(1)-C(15)-C(16)	112.62(15)
H(15A)-C(15)-H(15B)	108(2)
C(16)-C(15)-H(15A)	111.3(16)
C(16)-C(15)-H(15B)	109.2(16)
C(15)-C(16)-H(16A)	110.6(15)
C(15)-C(16)-H(16B)	109.0(14)
C(15)-C(16)-H(16C)	109.9(17)

H(16A)-C(16)-H(16B)	105(2)
H(16A)-C(16)-H(16C)	111(2)
H(16B)-C(16)-H(16C)	111(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for 002. The anisotropic displacement factor exponent takes the form: -2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	26(1)	27(1)	35(1)	-6(1)	-11(1)	18(1)
F(1)	15(1)	21(1)	10(1)	3(1)	1(1)	7(1)
N(1)	11(1)	15(1)	13(1)	0(1)	0(1)	4(1)
O(1)	15(1)	22(1)	13(1)	1(1)	1(1)	5(1)
C(1)	11(1)	15(1)	10(1)	1(1)	1(1)	4(1)
C(2)	11(1)	14(1)	14(1)	-1(1)	-1(1)	6(1)
C(3)	11(1)	15(1)	16(1)	-2(1)	1(1)	6(1)
C(4)	14(1)	22(1)	17(1)	-3(1)	-1(1)	9(1)
C(5)	13(1)	35(1)	23(1)	-9(1)	-2(1)	10(1)
C(6)	14(1)	31(1)	25(1)	-9(1)	5(1)	-2(1)
C(7)	24(1)	23(1)	22(1)	-1(1)	6(1)	-1(1)
C(8)	19(1)	18(1)	17(1)	0(1)	2(1)	4(1)
C(9)	11(1)	13(1)	12(1)	0(1)	0(1)	4(1)
C(10)	14(1)	16(1)	11(1)	-2(1)	0(1)	6(1)
C(11)	14(1)	19(1)	13(1)	-1(1)	-1(1)	6(1)
C(12)	14(1)	16(1)	19(1)	1(1)	-2(1)	7(1)
C(13)	19(1)	16(1)	21(1)	-6(1)	-4(1)	9(1)
C(14)	16(1)	16(1)	15(1)	-4(1)	-3(1)	6(1)
C(15)	15(1)	14(1)	17(1)	-1(1)	0(1)	6(1)
C(16)	23(1)	20(1)	27(1)	2(1)	-2(1)	13(1)

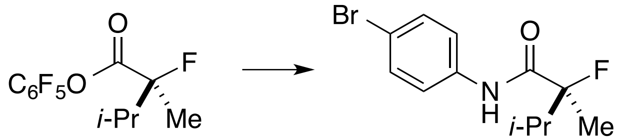
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 002.

	x	y	z	U(eq)
H(1)	12063(13)	3878(13)	-2590(50)	20(6)
H(4)	10969(14)	3429(14)	-4490(60)	27(6)
H(5)	9756(16)	2508(16)	-4680(60)	39(8)
H(6)	9342(13)	1631(14)	-1740(50)	24(6)
H(7)	10052(16)	1746(16)	1450(60)	34(8)
H(8)	11176(14)	2665(13)	2020(50)	25(6)
H(10)	13993(13)	5007(14)	4230(50)	21(6)
H(11)	14749(13)	4603(13)	5380(50)	22(6)
H(13)	14145(12)	3316(13)	-740(50)	16(5)
H(14)	13354(13)	3712(13)	-1780(50)	17(6)
H(15A)	13664(14)	5641(14)	1550(50)	24(6)
H(15B)	13023(13)	5218(13)	3220(50)	21(6)
H(16A)	12962(14)	5806(13)	-1430(50)	25(6)
H(16B)	12833(13)	6055(13)	1210(50)	21(6)
H(16C)	12244(17)	5258(17)	180(60)	41(8)

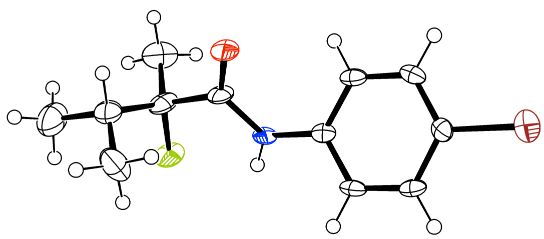
Table 6. Torsion angles [°] for 002.

Cl(1)-C(12)-C(13)-C(14)	177.93(14)
F(1)-C(1)-C(2)-N(1)	2.96(19)
F(1)-C(1)-C(2)-O(1)	-177.03(15)
F(1)-C(1)-C(9)-C(10)	137.30(15)
F(1)-C(1)-C(9)-C(14)	-44.17(19)
F(1)-C(1)-C(15)-C(16)	46.83(19)
N(1)-C(3)-C(4)-C(5)	177.70(16)
N(1)-C(3)-C(8)-C(7)	-176.77(18)
C(1)-C(9)-C(10)-C(11)	178.58(15)
C(1)-C(9)-C(14)-C(13)	-179.27(16)
C(2)-N(1)-C(3)-C(4)	153.40(17)
C(2)-N(1)-C(3)-C(8)	-29.4(3)
C(2)-C(1)-C(9)-C(10)	-106.49(17)
C(2)-C(1)-C(9)-C(14)	72.04(19)
C(2)-C(1)-C(15)-C(16)	-70.72(19)
C(3)-N(1)-C(2)-O(1)	-0.9(3)
C(3)-N(1)-C(2)-C(1)	179.13(15)
C(3)-C(4)-C(5)-C(6)	-1.0(3)
C(4)-C(3)-C(8)-C(7)	0.3(3)
C(4)-C(5)-C(6)-C(7)	0.8(3)
C(5)-C(6)-C(7)-C(8)	0.0(3)
C(6)-C(7)-C(8)-C(3)	-0.5(3)
C(8)-C(3)-C(4)-C(5)	0.4(3)
C(9)-C(1)-C(2)-N(1)	-112.40(16)
C(9)-C(1)-C(2)-O(1)	67.6(2)
C(9)-C(1)-C(15)-C(16)	165.67(15)
C(9)-C(10)-C(11)-C(12)	0.3(3)
C(10)-C(9)-C(14)-C(13)	-0.7(3)
C(10)-C(11)-C(12)-Cl(1)	-178.57(13)
C(10)-C(11)-C(12)-C(13)	0.0(3)
C(11)-C(12)-C(13)-C(14)	-0.6(3)
C(12)-C(13)-C(14)-C(9)	1.0(3)
C(14)-C(9)-C(10)-C(11)	0.0(2)
C(15)-C(1)-C(2)-N(1)	120.29(16)
C(15)-C(1)-C(2)-O(1)	-59.7(2)
C(15)-C(1)-C(9)-C(10)	17.9(2)
C(15)-C(1)-C(9)-C(14)	-163.54(15)

Symmetry transformations used to generate equivalent atoms:



(S)-N-(4-Bromophenyl)-2-fluoro-2,3-dimethylbutanamide (derived from the product of eq 3). (*S*)-Perfluorophenyl 2-fluoro-2,3-dimethylbutanoate (30 mg, 0.10 mmol; 73% ee, obtained with (–)-**PPY***), 4-bromoaniline (34 mg, 0.20 mmol), Et_3N (42 µL, 0.30 mmol), and THF (0.3 mL) were added to a 4-mL vial, which was then sealed and heated at 65 °C for 12 h. The mixture was then allowed to cool to room temperature, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexanes → 10% Et_2O in hexanes), which furnished the product as a white solid. The product was further purified by recrystallization from *n*-hexanes (>90% ee). X-ray quality crystals were obtained by slowly evaporating *n*-hexanes from a saturated solution of the amide in *n*-hexanes. The absolute stereochemistry was determined to be (*S*) by X-ray crystallography.



A crystal of $C_{12}H_{15}BrFNO$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Apex II diffractometer with filtered Mo-Kα radiation at a temperature of 100 K. The crystal was determined to be a two-component non-merohedral twin. Both components were integrated and the data processed with TWINABS. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339–341.

[2] SHELXS, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122.

[3] SHELXL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112–122.

Table 1. Crystal data and structure refinement for syl003.

Identification code	syl003	
Empirical formula	$C_{12} H_{15} Br F N O$	
Formula weight	288.16	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.4495(7) Å	α = 90°.
	b = 5.1247(4) Å	β = 95.193(4) °.
	c = 14.4009(12) Å	γ = 90 °.
Volume	621.02(9) $Å^3$	
Z	2	
Density (calculated)	1.541 Mg/m^3	
Absorption coefficient	3.301 mm^{-1}	
F(000)	292	
Crystal size	0.25 x 0.24 x 0.08 mm^3	
Theta range for data collection	2.420 to 26.371°.	
Index ranges	-10<=h<=10, -6<=k<=6, -17<=l<=18	
Reflections collected	23534	
Independent reflections	2470	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.862085 and 0.634353	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2470 / 1 / 149	
Goodness-of-fit on F^2	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0842	
R indices (all data)	R1 = 0.0361, wR2 = 0.0856	
Absolute structure parameter (Flack)	0.021(6)	
Largest diff. peak and hole	0.659 and -0.544 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for syl003. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

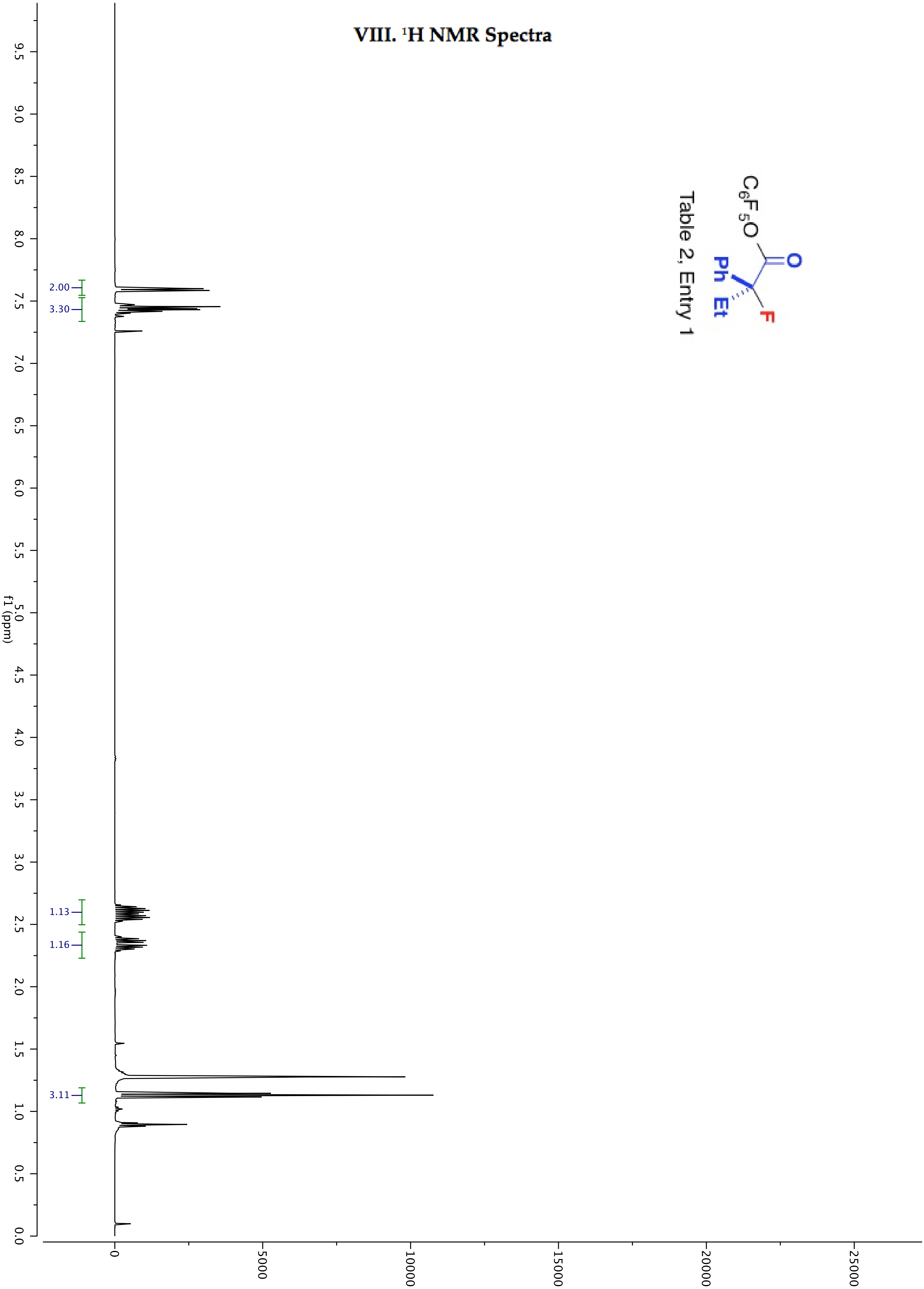
	x	y	z	U(eq)
Br(1)	6518(1)	6703(2)	7272(1)	39(1)
F(1)	8681(6)	3998(8)	1596(3)	40(1)
O(1)	8051(7)	9638(9)	2920(4)	38(1)
N(1)	8106(7)	5310(11)	3272(4)	25(1)
C(9)	8147(8)	7862(12)	5679(5)	23(1)
C(7)	7805(8)	5592(12)	4220(5)	20(1)
C(8)	8490(8)	7585(12)	4765(5)	24(2)
C(1)	8216(9)	7372(10)	2693(6)	29(2)
C(11)	6450(8)	4068(12)	5525(5)	24(1)
C(12)	6810(8)	3804(12)	4613(5)	24(1)
C(2)	8620(8)	6720(20)	1691(4)	34(2)
C(4)	7261(12)	7717(14)	1007(6)	40(2)
C(5)	5694(9)	6660(40)	1196(5)	49(2)
C(10)	7113(8)	6135(11)	6043(4)	23(2)
C(3)	10267(11)	7688(17)	1567(7)	50(2)
C(6)	7660(14)	7130(30)	4(6)	60(3)

Table 3. Bond lengths [Å] and angles [°] for syl003.

Br(1)-C(10)	1.906(7)
F(1)-C(2)	1.404(11)
O(1)-C(1)	1.218(8)
N(1)-C(7)	1.420(9)
N(1)-C(1)	1.355(8)
C(9)-C(8)	1.381(10)
C(9)-C(10)	1.379(9)
C(7)-C(8)	1.383(9)
C(7)-C(12)	1.396(10)
C(1)-C(2)	1.548(10)
C(11)-C(12)	1.382(10)
C(11)-C(10)	1.385(9)
C(2)-C(4)	1.532(11)
C(2)-C(3)	1.503(11)
C(4)-C(5)	1.479(13)
C(4)-C(6)	1.542(12)
C(1)-N(1)-C(7)	122.8(6)
C(10)-C(9)-C(8)	119.4(6)
C(8)-C(7)-N(1)	121.2(6)
C(8)-C(7)-C(12)	119.4(6)
C(12)-C(7)-N(1)	119.3(6)
C(9)-C(8)-C(7)	120.2(6)
O(1)-C(1)-N(1)	124.2(7)
O(1)-C(1)-C(2)	119.8(7)
N(1)-C(1)-C(2)	116.0(6)
C(12)-C(11)-C(10)	118.3(6)
C(11)-C(12)-C(7)	120.8(6)
F(1)-C(2)-C(1)	108.6(6)
F(1)-C(2)-C(4)	107.5(6)
F(1)-C(2)-C(3)	105.8(6)
C(4)-C(2)-C(1)	108.2(6)
C(3)-C(2)-C(1)	108.9(7)
C(3)-C(2)-C(4)	117.5(7)
C(2)-C(4)-C(6)	108.8(8)
C(5)-C(4)-C(2)	113.0(7)
C(5)-C(4)-C(6)	112.2(8)
C(9)-C(10)-Br(1)	118.9(5)
C(9)-C(10)-C(11)	121.7(6)
C(11)-C(10)-Br(1)	119.3(5)

Symmetry transformations used to generate equivalent atoms:

VIII. ^{1}H NMR Spectra



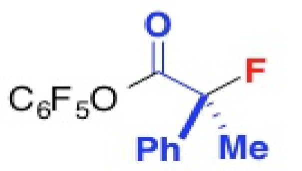
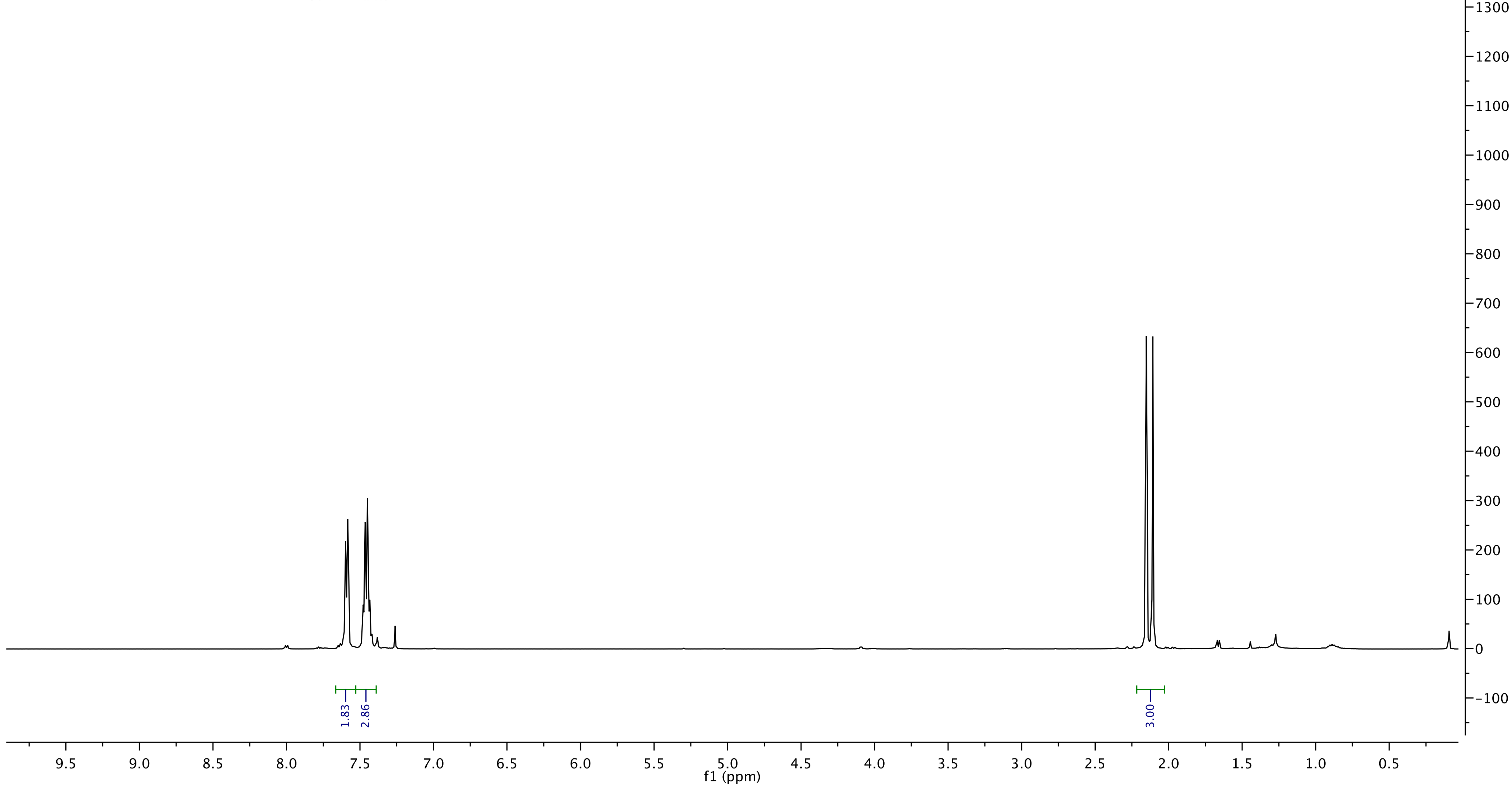
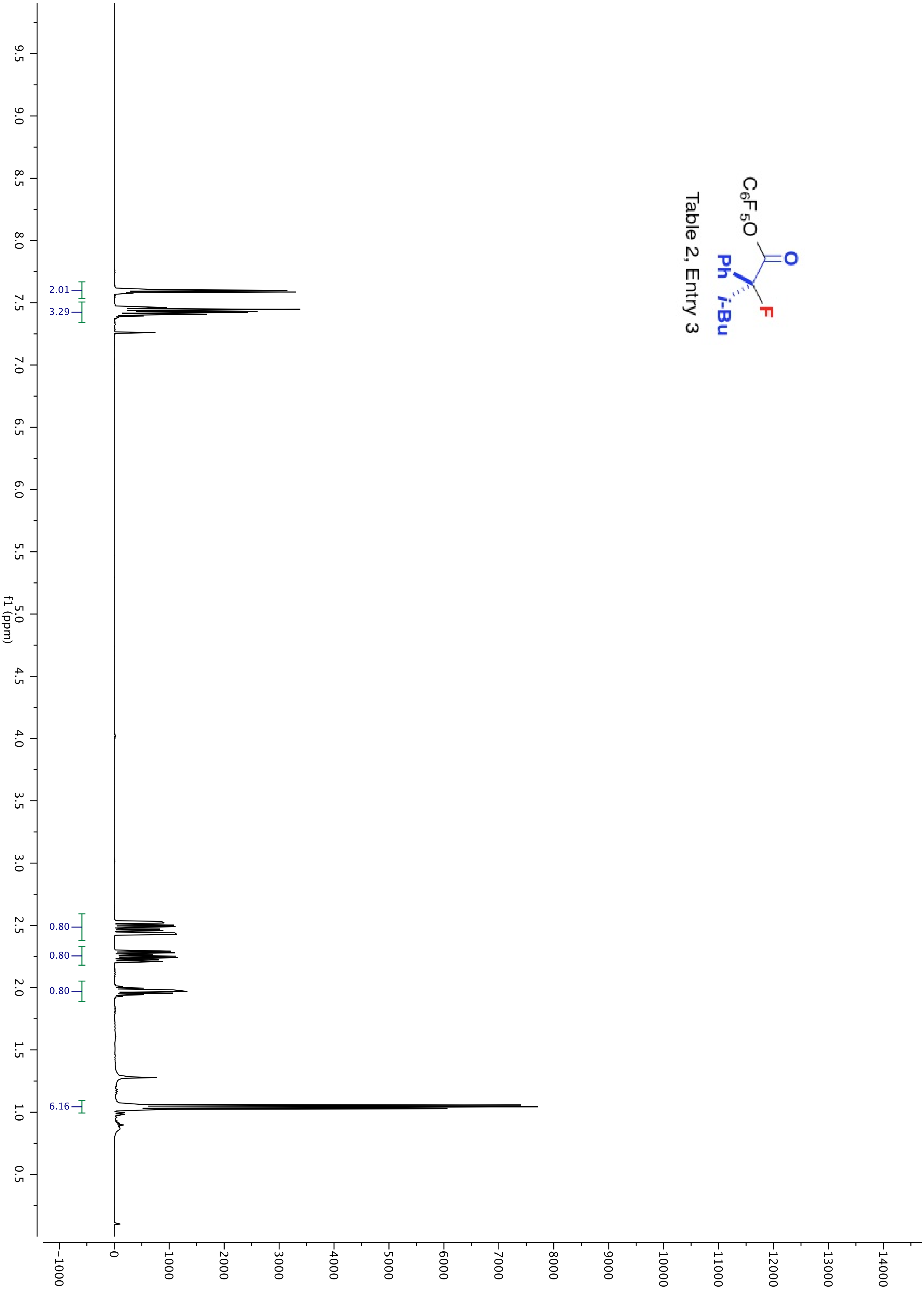
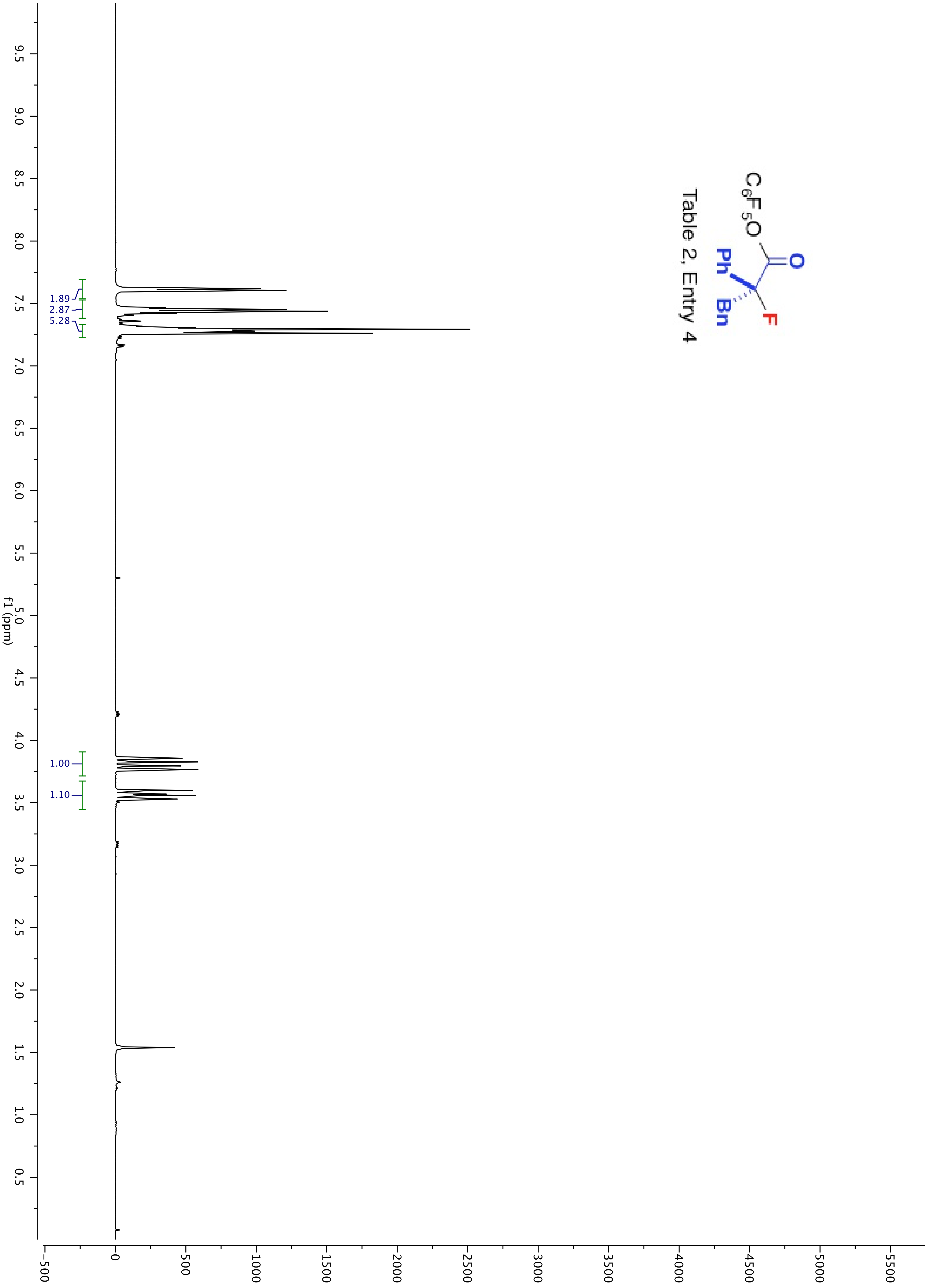


Table 2, Entry 2

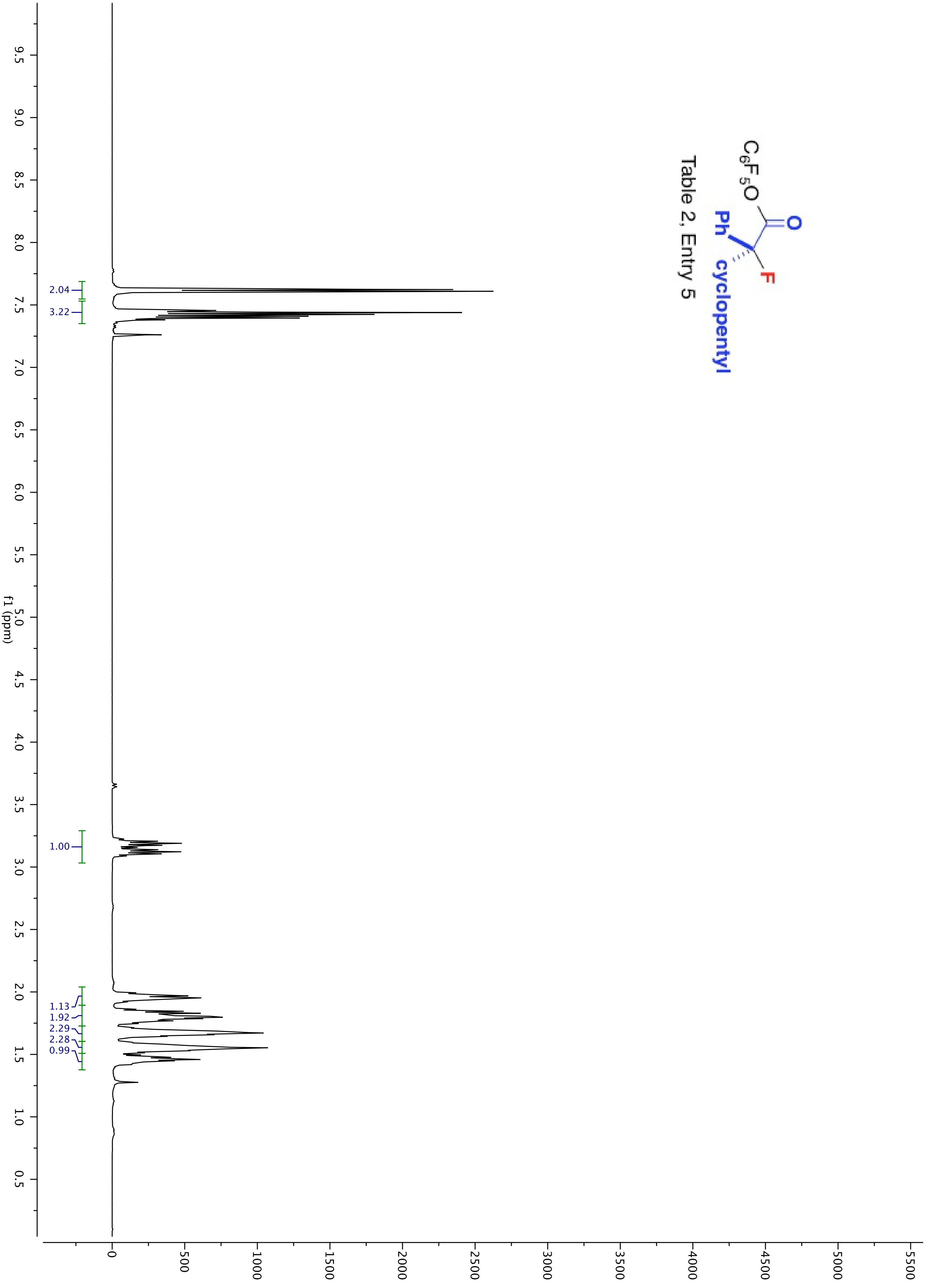




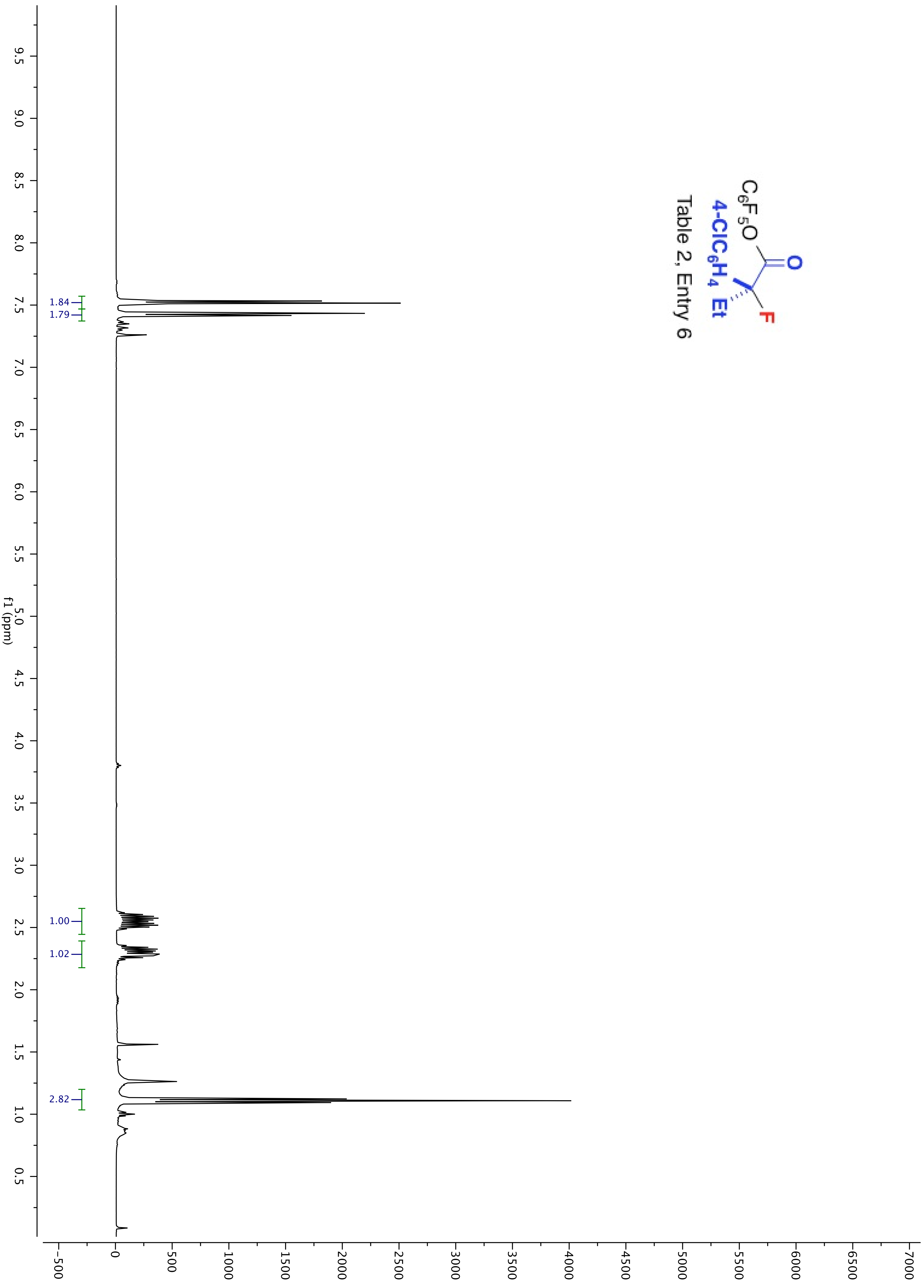
C_6F_5O
O
F
Ph
i-Bu
Table 2, Entry 3
2.01
3.29
0.80
0.80
0.80
6.16
f1 (ppm)



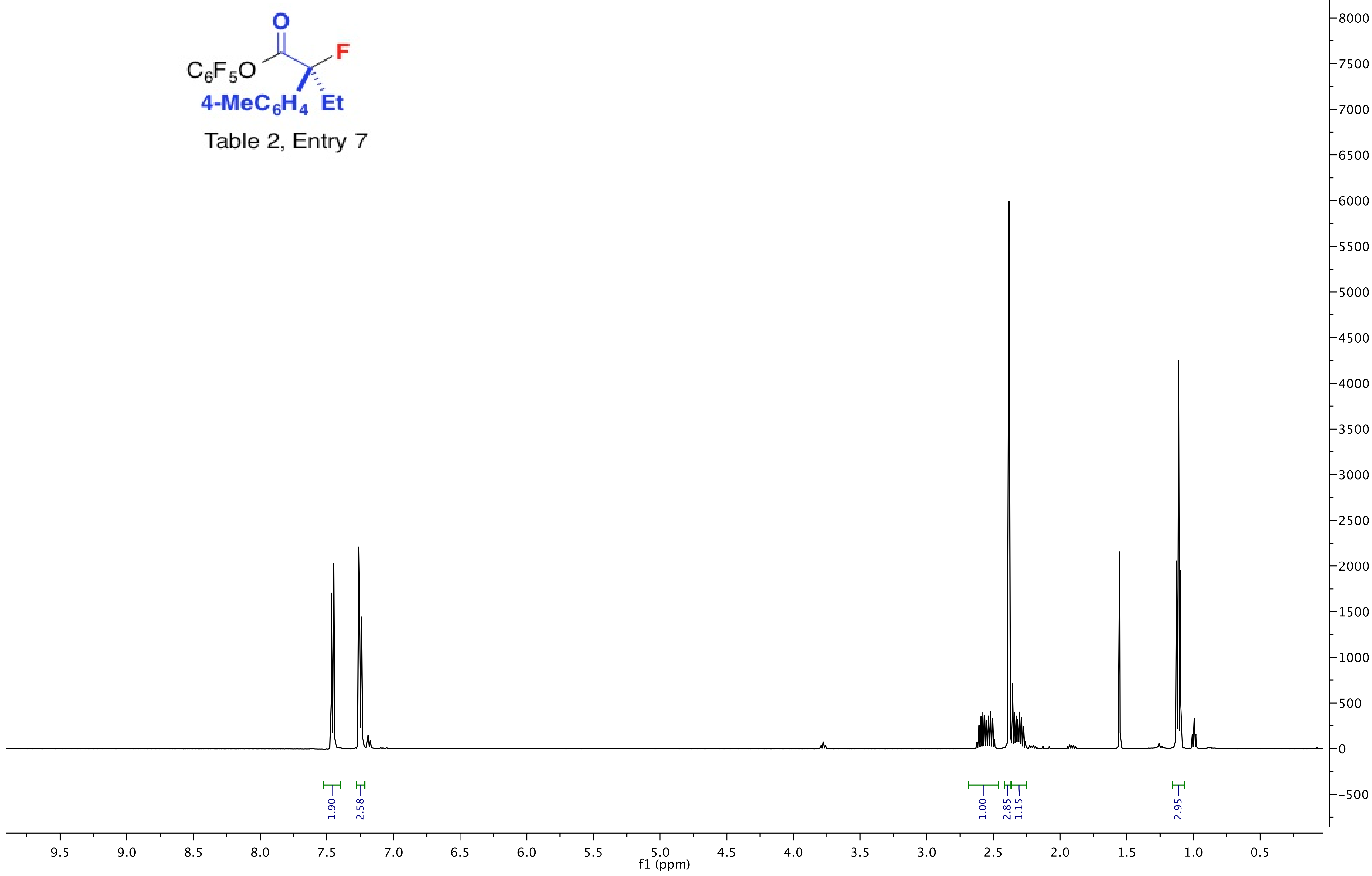
C_6F_5O
O
F
Ph
Bn
Table 2, Entry 4
f1 (ppm)
1.89
2.87
5.28
1.00
1.10

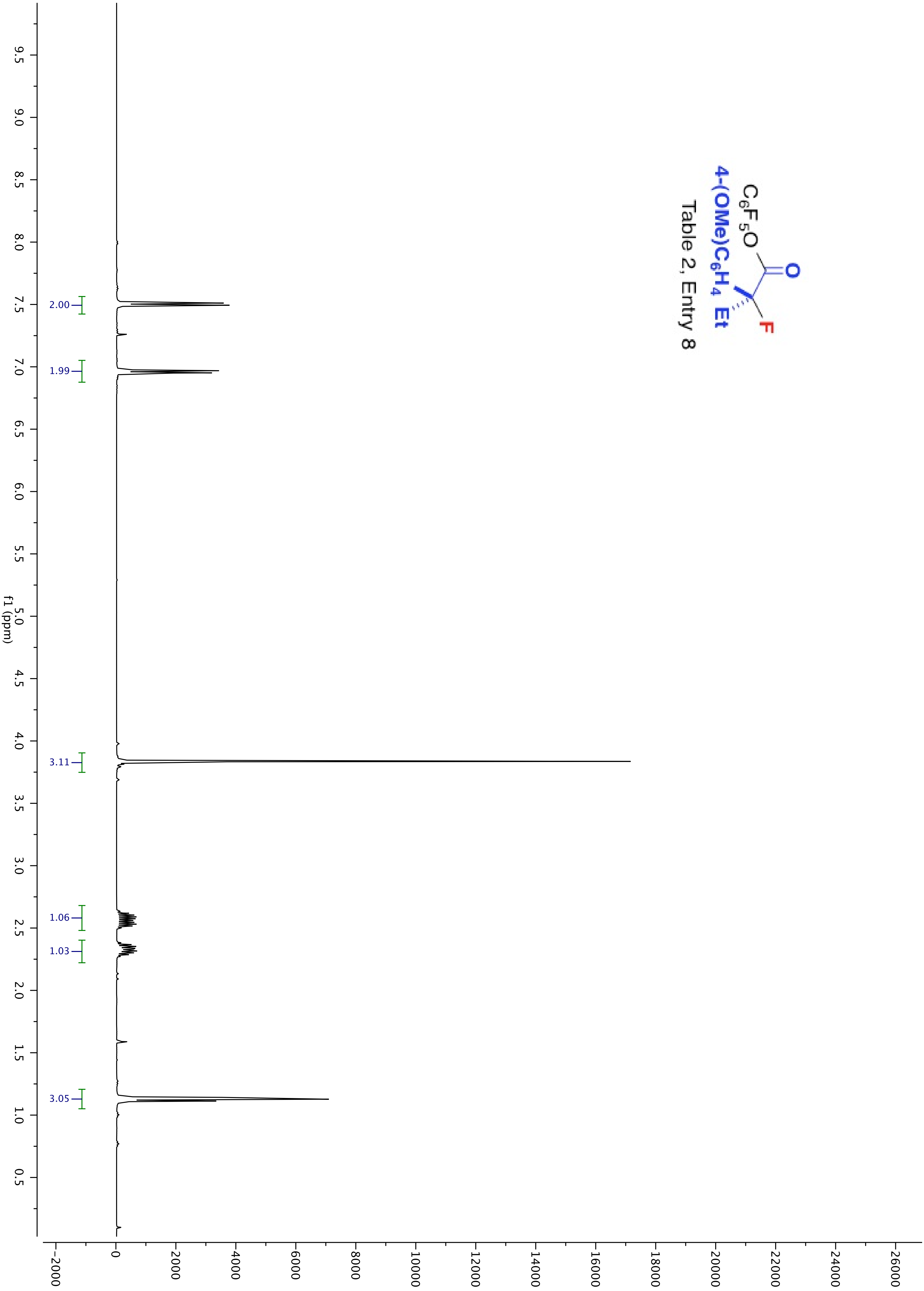


C_6F_5O
O
F
Ph
cyclopentyl
Table 2, Entry 5
2.04
3.22
1.00
1.13
1.92
2.29
2.28
0.99
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500



C6F5O
O
F
4-ClC6H4
Et
Table 2, Entry 6
f1 (ppm)
1.84
1.79
1.00
1.02
2.82


O
F
C6F5O
4-MeC6H4 Et
Table 2, Entry 7
1.90
2.58
1.00
2.85
1.15
2.95
f1 (ppm)


C6F5O
O
F
4-(OMe)C6H4
Et
Table 2, Entry 8
f1 (ppm)
2.00
1.99
3.11
1.06
1.03
3.05

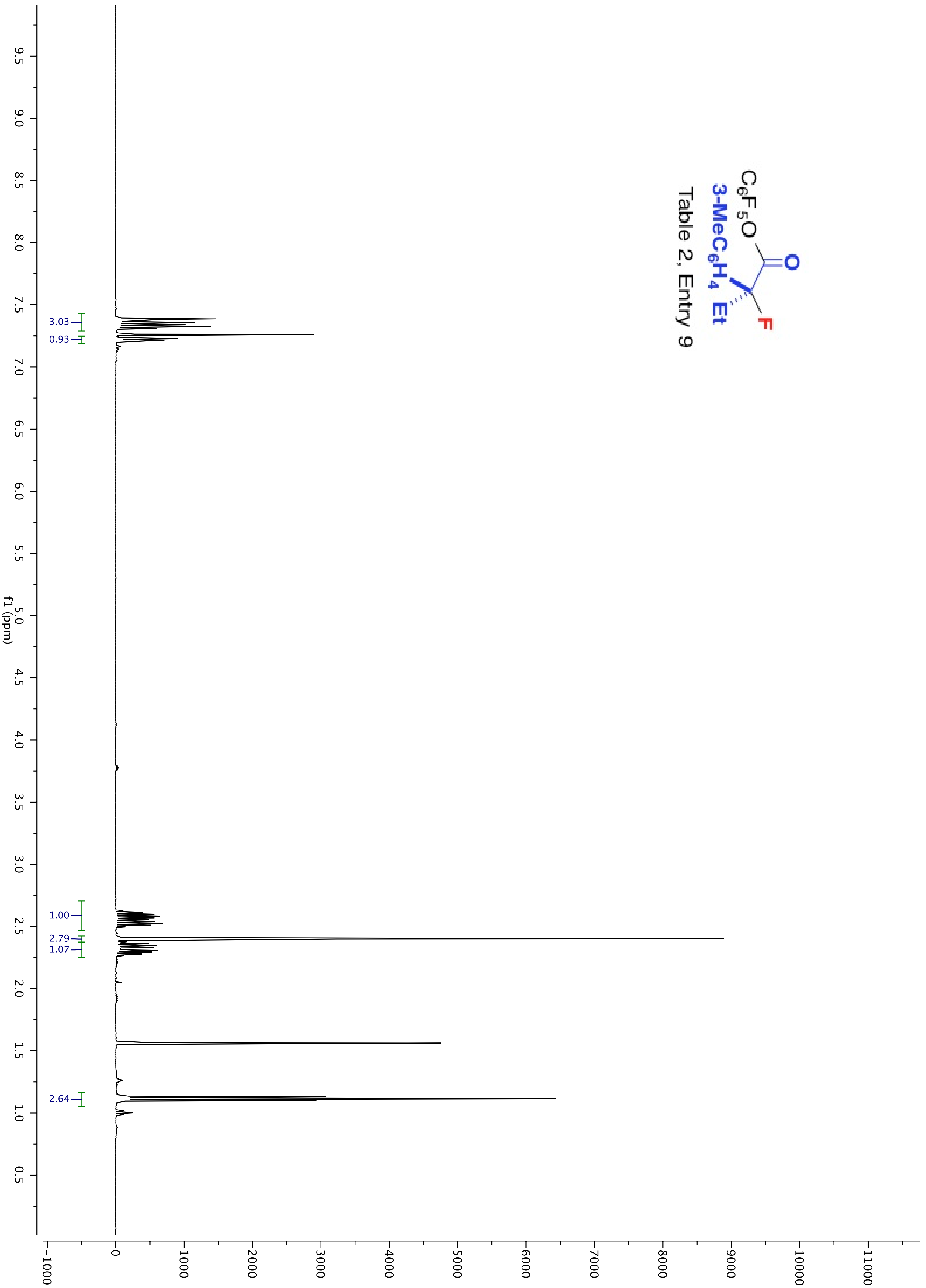


Table 2, Entry 9
f1 (ppm)
3.03
0.93
1.00
2.79
1.07
2.64

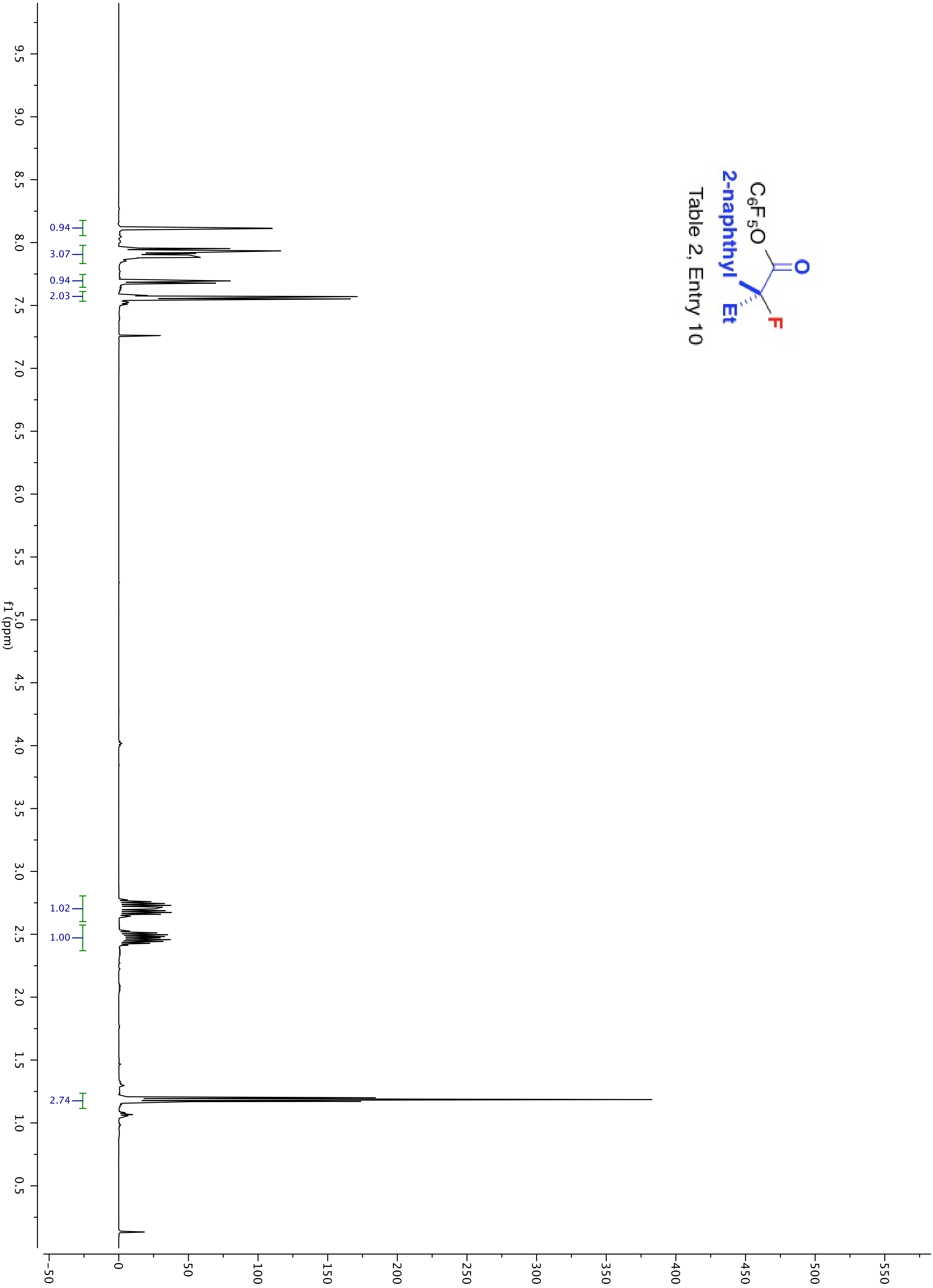
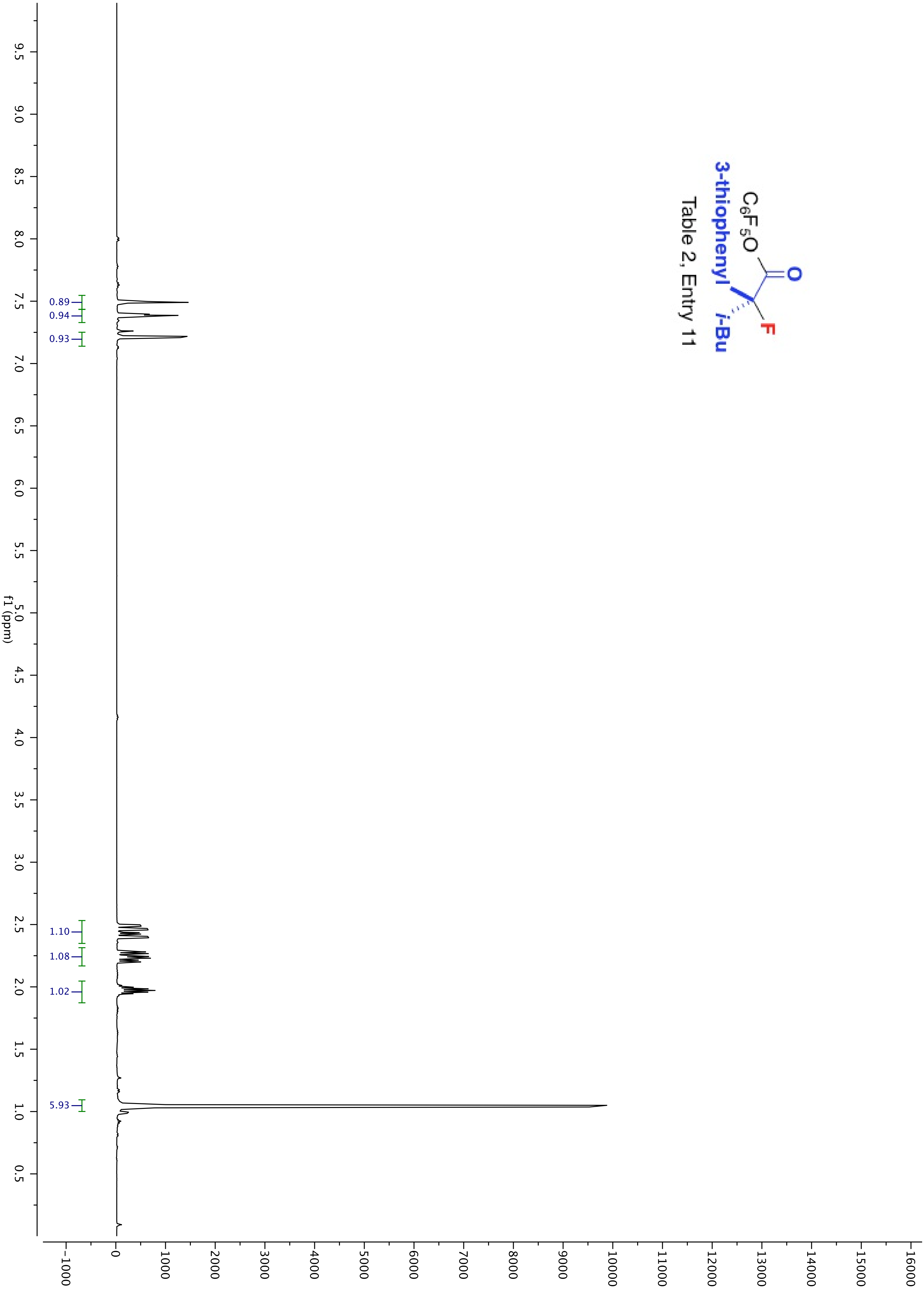
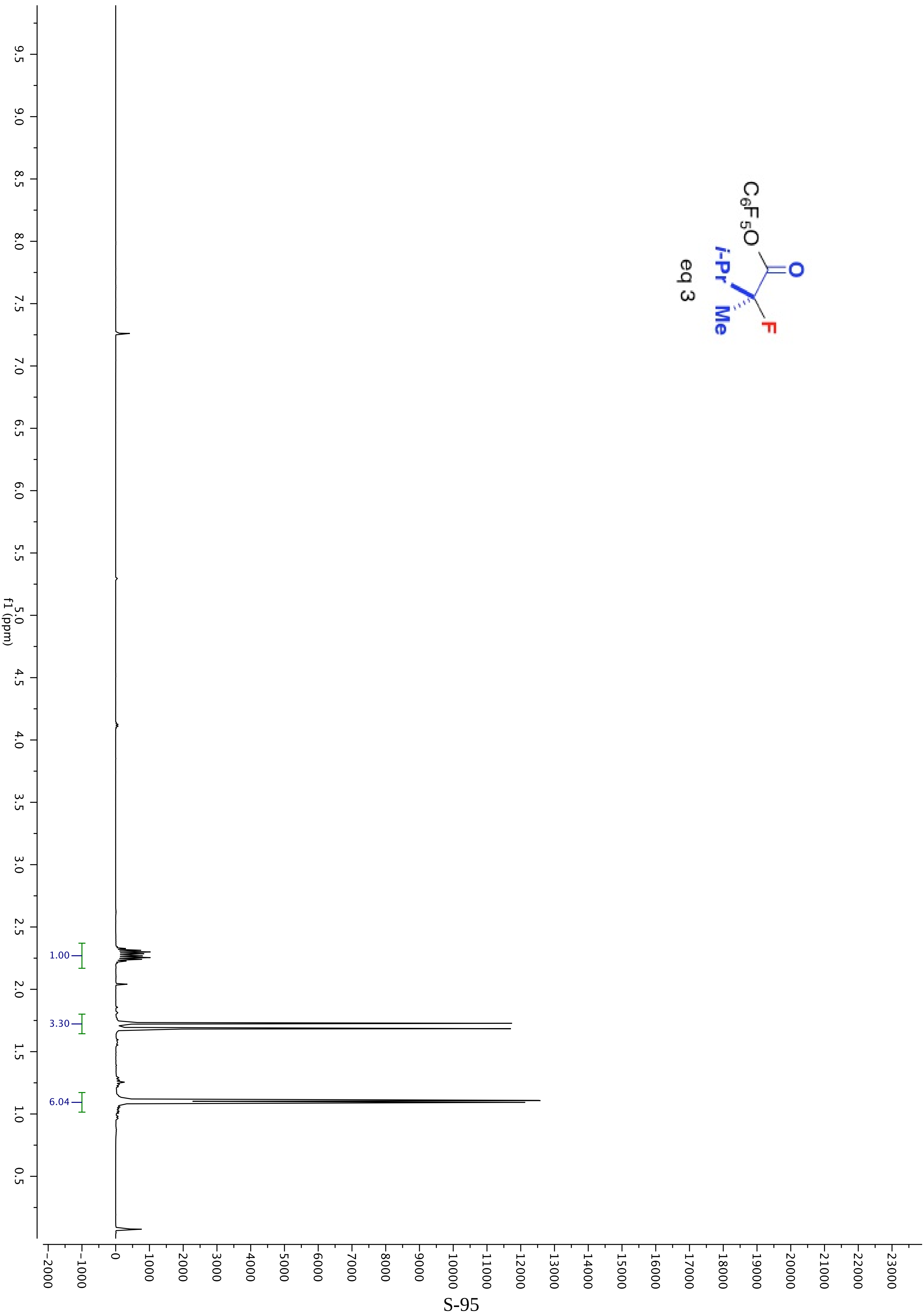
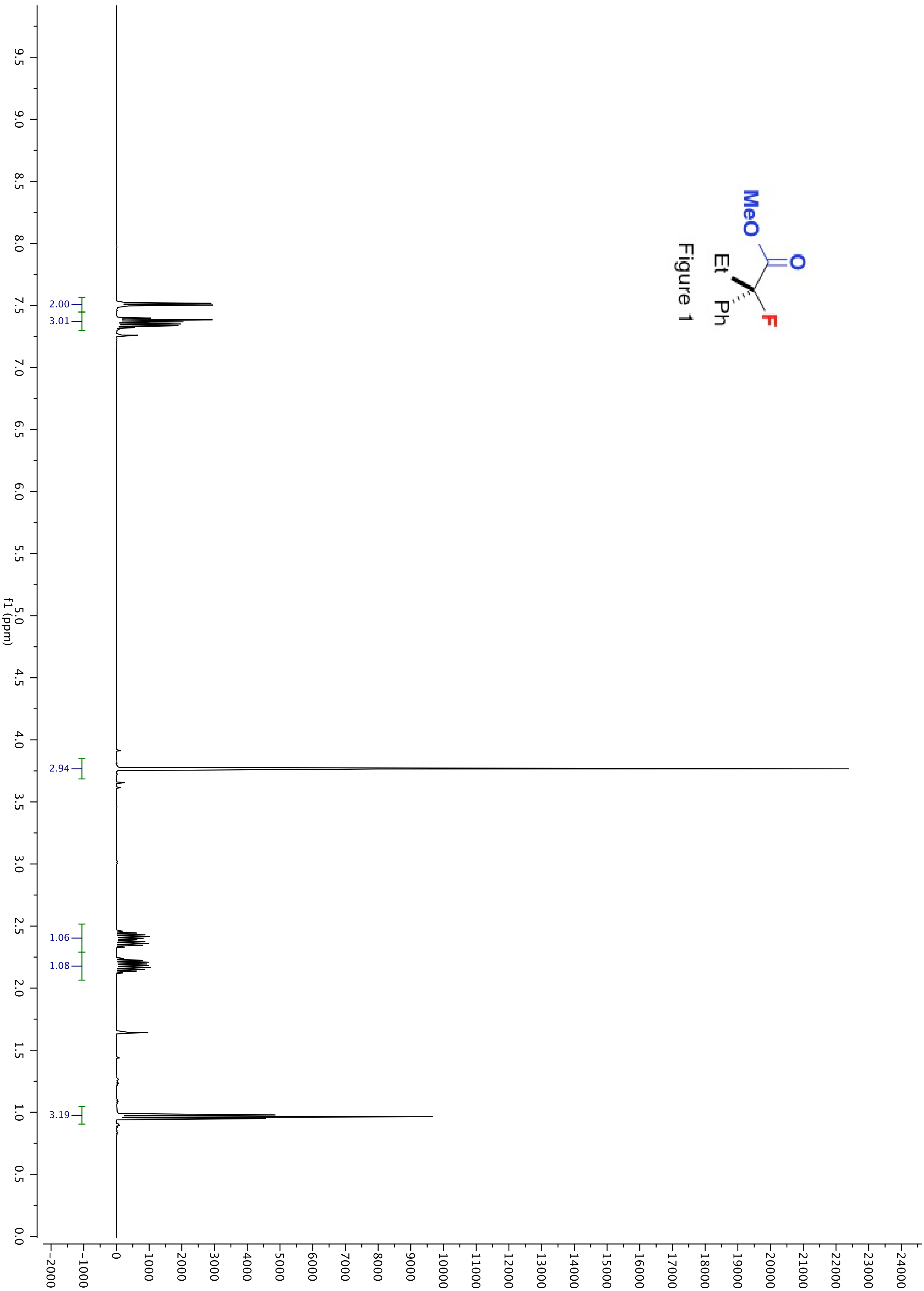


Table 2, Entry 10
2-naphthyl
Et
F
O
f1 (ppm)


C6F5O
O
F
3-thiophenyl
i-Bu
Table 2, Entry 11
f1 (ppm)
0.89
0.94
0.93
1.10
1.08
1.02
5.93


C6F5O
O
F
i-Pr
Me
eq 3
f1 (ppm)
1.00
3.30
6.04


MeO
O
F
Et
Ph
Figure 1
2.00
3.01
2.94
1.06
1.08
3.19
f1 (ppm)

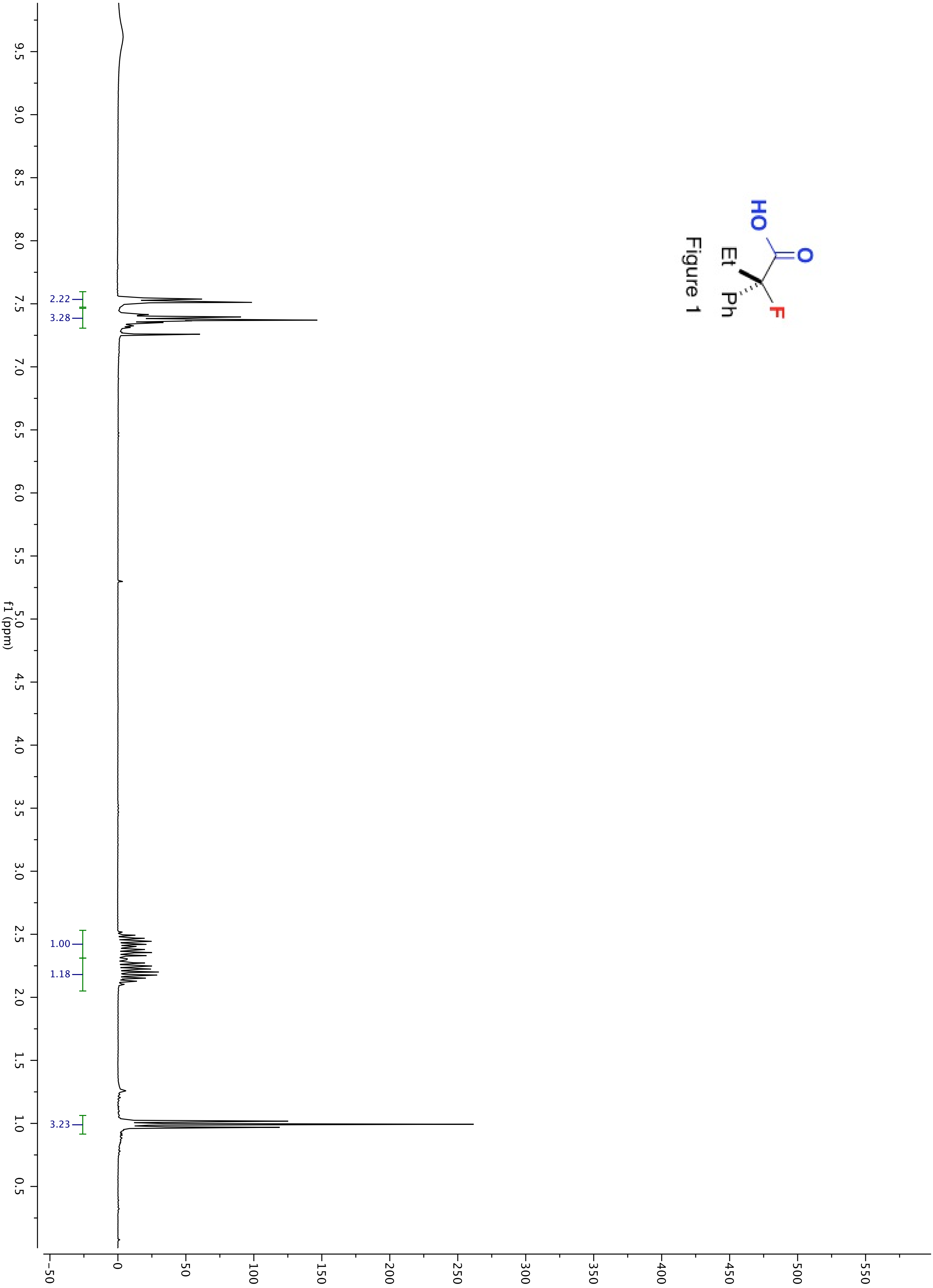

HO
O
F
Et
Ph
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2.22
3.28
1.00
1.18
3.23
-50
0
50
100
150
200
250
300
350
400
450
500
550

Figure 1

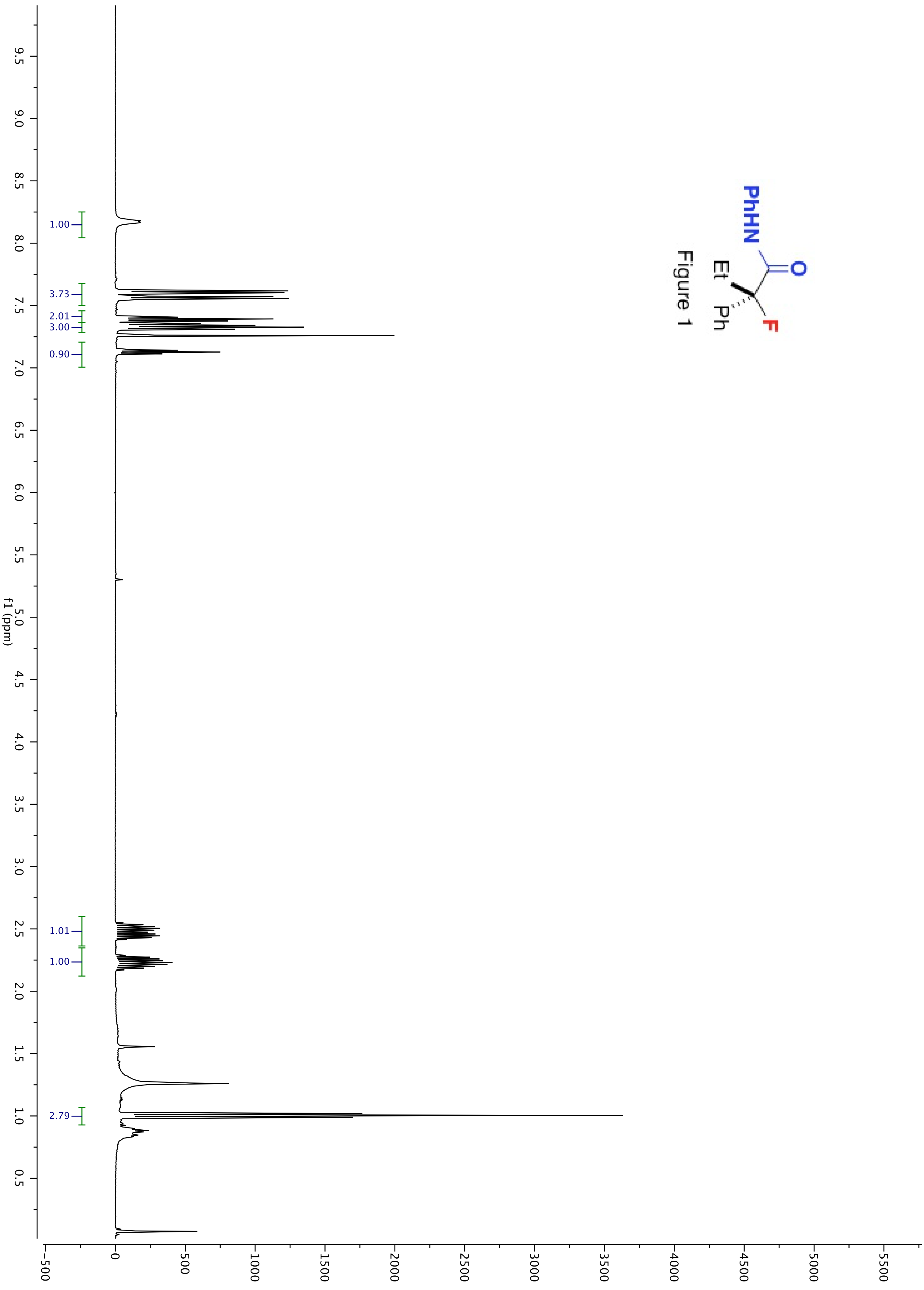


Figure 1

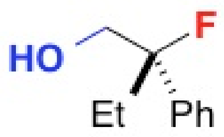
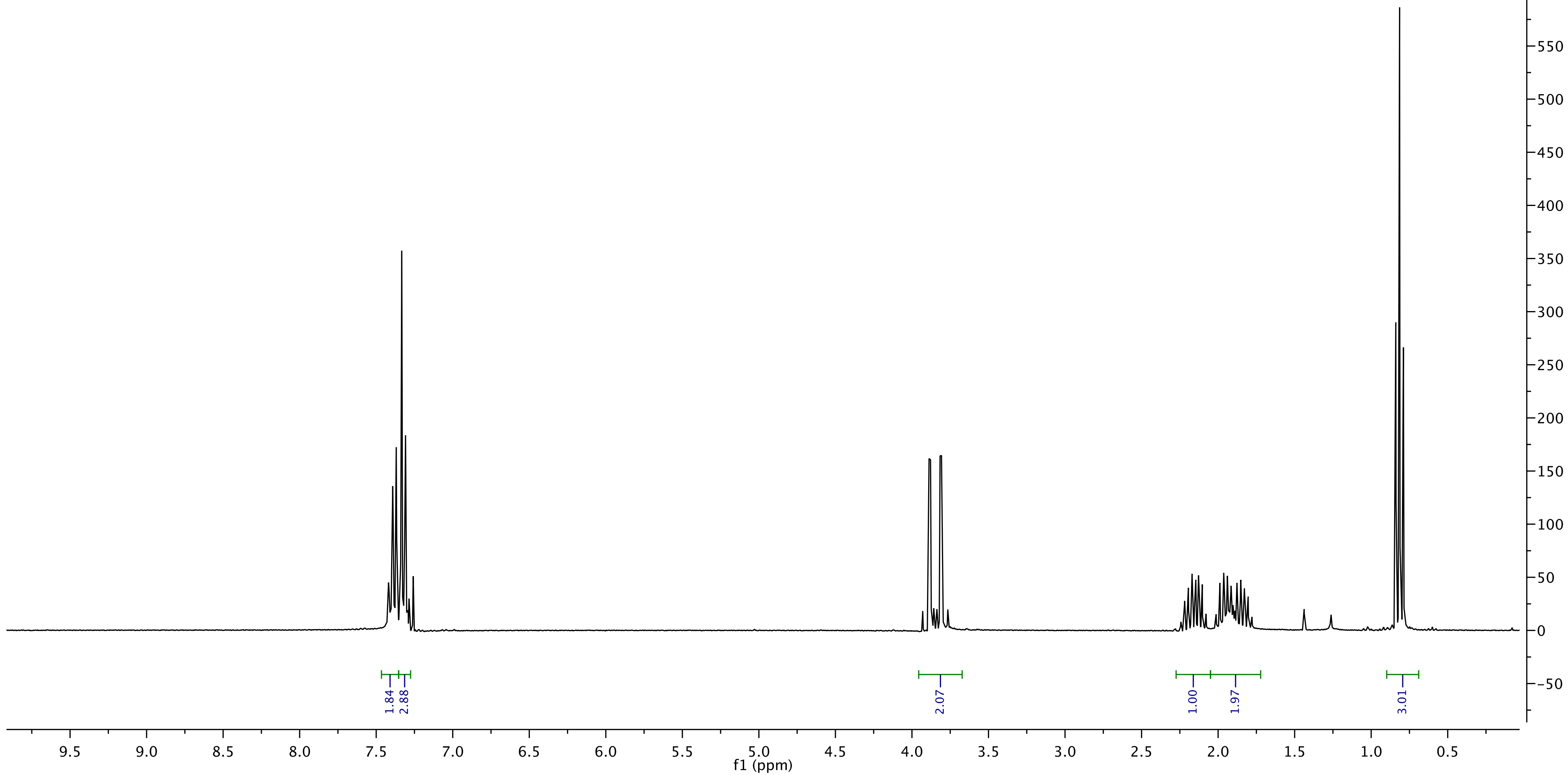
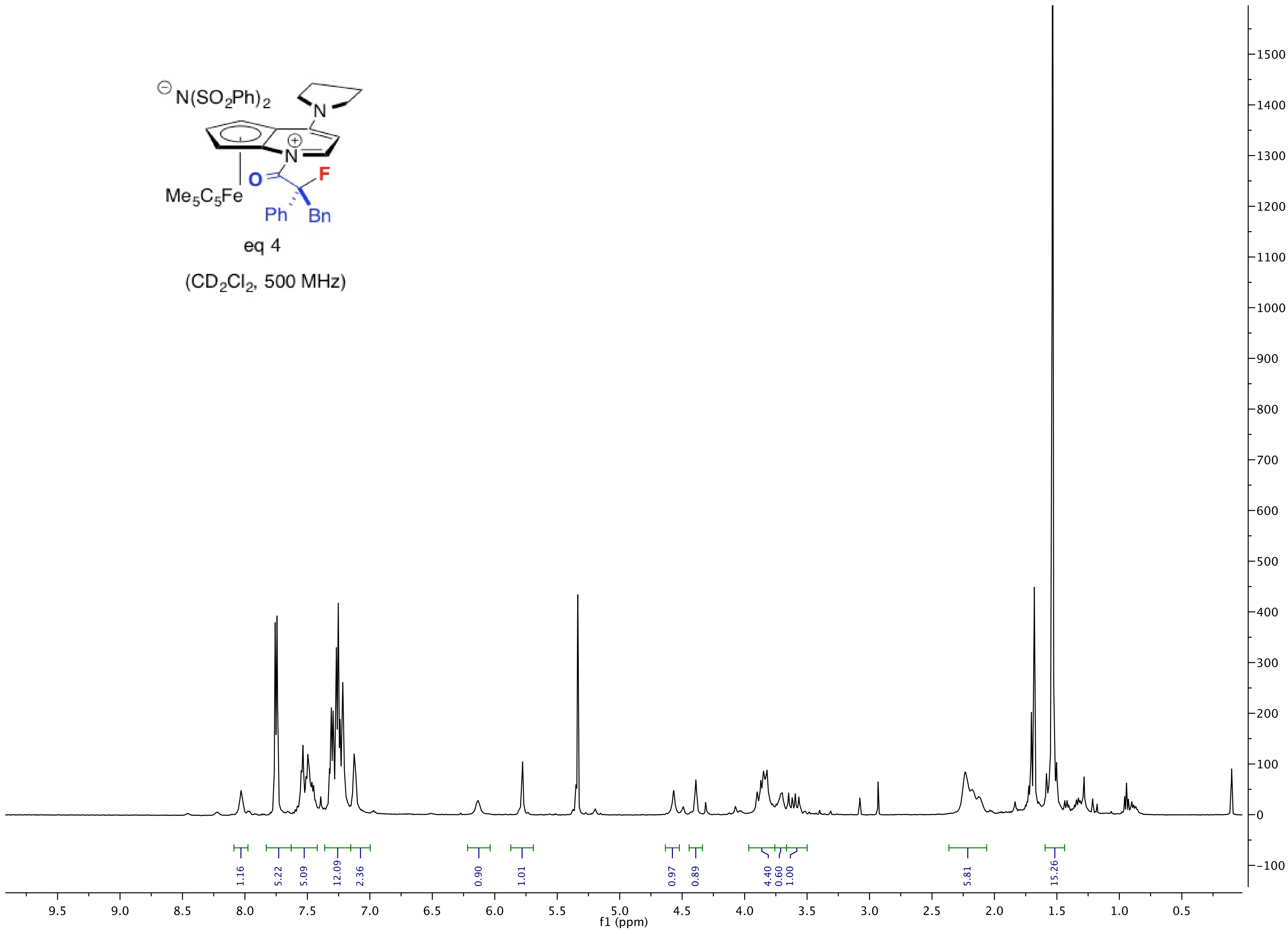


Figure 1




N(SO2Ph)2
Me5C5Fe
O
F
N
Ph
Bn
eq 4
(CD2Cl2, 500 MHz)
1.16
5.22
5.09
12.09
2.36
0.90
1.01
0.97
0.89
4.40
0.60
1.00
5.81
15.26
f1 (ppm)

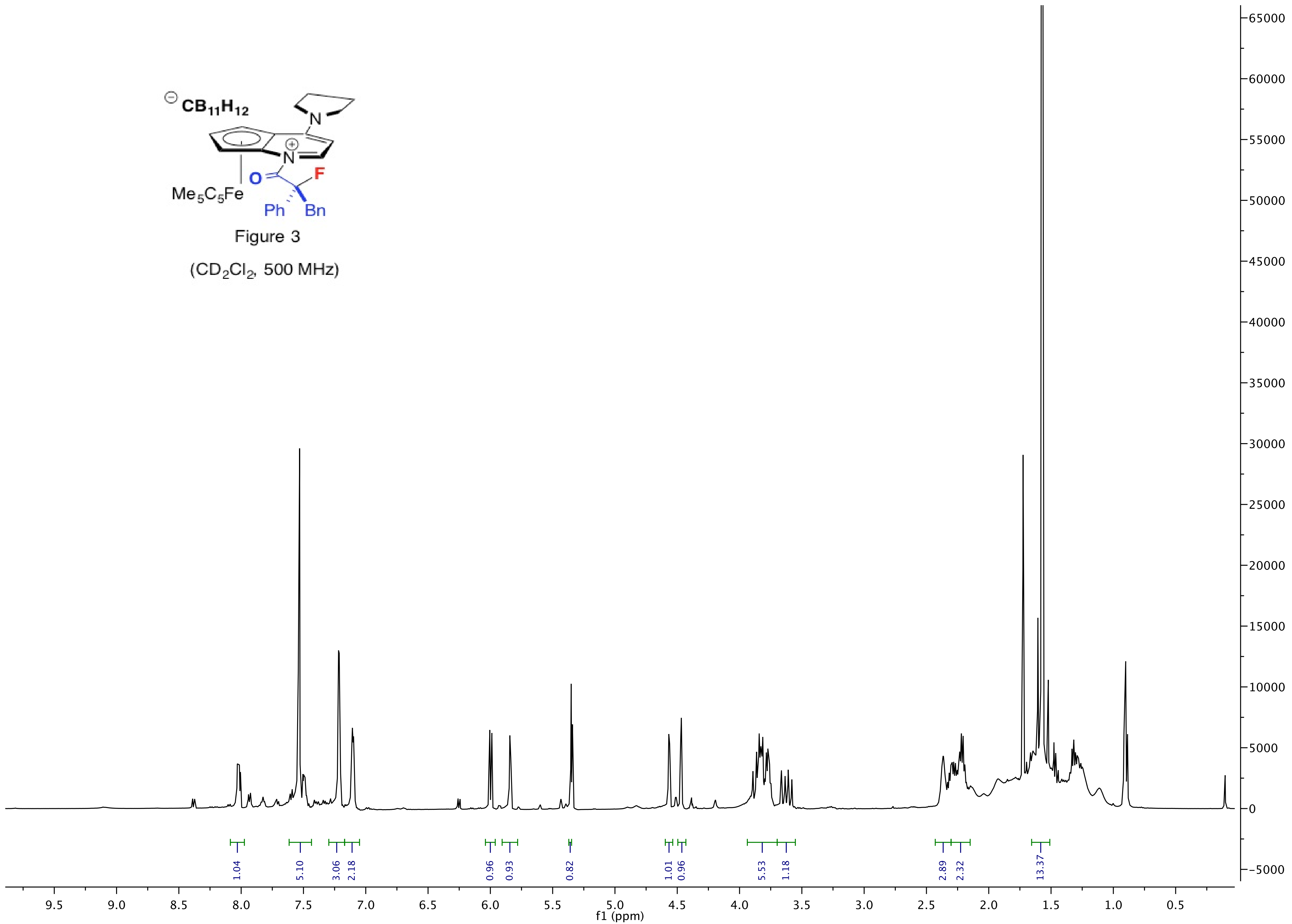


Figure 3

(CD_2Cl_2, 500 MHz)